PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

I. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE*.

III.

A few special Cryogens and Cryohydrates.

I HAVE, in the first place, to redeem the promise given in § 89, and, by discussing the behaviour as cryogens and cryohydrates of a few peculiar salts, to complete one part of my undertaking.

§ 105. *Chloride of Calcium as a Cryogen.* A. *Crystallized* $CaCl_2 + 3H_2O$.—The heat liberated when anhydrous $CaCl_2$ is brought into contact with water interferes with, by diminishing, the manifestation of cold due to the proper liquefaction of the salt and of the ice when the two are brought together. Accordingly in experiments with chloride of calcium as a cryogen which are to serve as a guide to the temperature at which the formation of the cryohydrate may be predicted, we may conveniently begin with the crystallized salt. A seasonable fall of snow last winter enabled me to extend my experiments with the chloride of calcium, not only in regard to the relative quantity of the two constituents, but to the relative effects of snow and pounded ice, and to establish conclusively that the two are of quite equal power when used as one element of a

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cryogen. The crystallized $CaCl_2 + 3\,H_2\,O$ was finely powdered and placed in weighed quantities on the weighed snow or crushed ice in a beaker, the two being stirred continuously with the thermometer. Under these conditions the lowest temperature is quickly reached.

TABLE XII.—Column (1) the weight in grammes of the powdered $CaCl_2 + 3\,H_2\,O$, column (2) the weight in grammes of the powdered ice or snow, columns (3) and (4) the respective percentages of the two, column (5) the temperature.

(1) $CaCl_2+3H_2O$, grammes.	(2) Snow or ice, grammes.	(3) Per cent., $CaCl_2+3H_2O$	(4) Per cent., snow or ice.	(5) Temperature, Centigrade.
100	33 snow	75	25	−21°
100	50 snow	66·6	33·3	−28
94	60 ice	61·5	38·5	−33
* 75	50 snow	60	40	−32
* 75	50 ice	60	40	−32
50	75 snow	40	60	−27
* 50	100 snow	33·3	66·6	−24
* 50	100 ice	33·3	66·6	−24·5

From this, especially from the examples marked *, it appears that snow and ice are of equal value as elements of cryogens, and that the greatest cold is obtained on mixing 38·5 of ice or snow with 61·5 of the crystallized salt. This is the ratio between $CaCl_2\,3\,H_2\,O$ and $5{\cdot}74\,H_2\,O$, or $4(CaCl_2\,3\,H_2\,O)$ and $23\,H_2\,O$ or $CaCl_2$ and $8{\cdot}74\,H_2\,O$.

§ 106. B. *Anhydrous* $CaCl_2$ *as Cryogen.*—Freshly fused $CaCl_2$ was finely powdered and mixed with finely crushed ice.

TABLE XIII.—Columns (1) and (2) show the actual quantities, in grammes, taken of $CaCl_2$ and ice respectively; columns (3) and (4) show the percentages; column (5) shows the lowest temperature reached; and the numbers in column (6) show the temperature to which the mixture rose after all the ice was melted in those cases where the proportion of ice was least.

(1) $CaCl_2$, grammes.	(2) Ice, grammes.	(3) $CaCl_2$, per cent.	(4) Ice, per cent.	(5) Lowest temp. Cent.	(6) Rose to temp. Cent.
50	50	50·0	50·0	+33°	
50	75	40·0	60·0	+10 to	+18°
50	90	35·7	64·3	+ 4 „	+14
50	95	34·5	65·5	+ 3 „	+11
50	100	33·3	66·7	− 2 „	+ 9
50	125	28·6	71·4	−10	
33·3	100	25·0	75·0	−13	
25	100	20·0	80·0	−15	
20	100	16·7	83·3	−14·5	
16·6	100	14·2	85·8	−12	
20	140	12·5	87·5	−12	

Here the lowest temperature is reached at the ratio 1 : 4, or about $CaCl_2 + 15\,H_2O$. We must not attach too much importance to the numbers of this Table, because, as before remarked, the liberation of heat when the anhydrous salt dissolves in, or rather combines with water, largely supplies heat for the liquefaction of the solid ice and salt. And accordingly, though the heat-quantity concerned may be deduced from knowledge of the quantity due to such combination and the specific heat of the solution and the heat of liquefaction of the ice, yet the temperature or heat-tension, being a function of the time or rate of liquefaction, cannot be so deduced. The caking of the chloride is also a source of experimental difficulty.

§ 107. *Monohydrated Chloride of Calcium as a Cryogen.*—On baking the terhydrate of chloride of calcium a porous mass is left, which is used for the absorption of water in gases. This, though called anhydrous in commerce, contains about one molecule of water. And the presence of the water is betrayed when the body is used as a cryogen. The chloride, finely powdered, was weighed upon snow or ice and stirred with the thermometer unceasingly. The higher ratios of frozen

water were ice, the lower ones were snow; the two are connected together at the 50 per cent. ratios, marked *.

TABLE XIV.

$CaCl_2+H_2O$, grammes.	Snow or ice, grammes.	$CaCl_2H_2O$, per cent.	Snow or ice, per cent.	Temperature, Centigrade.
100	33 snow	75	25	+ 5
100	50 ,,	66·7	33·3	− 4
75	50 ,,	60	40	−10
*50	50 ,,	50	50	−17
*50	50 ice	50	50	−17
50	100 ,,	33·3	66·7	−17
50	150 ,,	25	75	−16
50	200 ,,	20	80	−16
50	300 ,,	14·3	85·7	−16
50	400 ,,	11·1	88·9	−12
50	600 ,,	7·7	92·3	−10

The margin of ratio for minimum temperature is considerable. The minimum temperature itself is intermediate between the minima for $CaCl_2$ and $CaCl_2+3H_2O$.

§ 108. *The Cryohydrate of Chloride of Calcium.*—A solution of $CaCl_2\,3H_2O$, saturated at the temperature of the air (10° C.), was cooled to −20° in snow and ice. The mother-liquor was then exposed to the carbonic-acid-and-ether cryogen. The temperature sank to −37° C. under continual separation of a transparent hydrate. At −37° C. an opaque cryohydrate is formed, and the temperature remains constant for a considerable time. The opaque crystals, on being remelted, showed the following composition. By a silver-determination 6·6835 contained 2·3365 of $CaCl_2$. This shows 36·45 of $CaCl_2$, and exhibits the molecular ratio

$$CaCl_2+11{\cdot}8\,H_2O.$$

Mixed Salts, as Cryogens and Cryohydrates.

§ 109. Still bearing in mind the problem of sea-water, we may next consider the behaviour of mixtures of soluble salts, both as cryogens and cryohydrates. Even regarding salts as preserving the individuality of their metallic and non-metallic parts when mixed together, there is a variety of recomposition possible. Thus taking the typical salts AX and BY, we may

have A=B or X=Y. No double recomposition is possible in either of the latter cases. But there may still be formed double salts in which each metal is engaged with both non-metallic constituents. I suppose that in the present state of chemical knowledge it would be unwise to assert that any double salt is impossible, especially after the evidence which has been so abundantly given above that the body water is virtually pantameric.

On the other hand, remembering the liberal margin of ratio between ice and a salt for the production of the normal or maximum cold, we shall get by examining the temperature of the cryogen of a mixture of salts and the temperature of their common cryohydrate, if they have one, a valuable and indeed unique insight into their molecular relation, in the sense of determining whether double salts or double recomposition ensues. At present I have confined my examination to the various cases of two salts. Of these a few typical examples are taken; and in the first place a pair of salts are examined which differ only in their metals.

§ 110. *Mixed Nitrates of Potassium and Sodium as Cryohydrate.*—The salts were just fused, poured on a slab, crushed while hot, and bottled. The two salts were weighed in monomolecular ratio; namely, of

KNO_3 there were 33·666 grms.
$NaNO_3$ „ 28·333 „

These quantities were mixed, completely dissolved in water, and allowed to evaporate at 13° C. till crystallization began. The mixture was then cooled in an ice-salt cryogen. At about +12° to +10° C. transparent crystals resembling KNO_3 began to form, and continued to do so as the temperature fell. At about −7° an opaque cryohydrate appeared. This went on till −10° C. was reached, when the whole was pasty. At −13° the mass was not yet dry. At −14°·5 it was nearly dry. At −16°·5 to −17° it became perfectly dry. We find then that

The cryohydrate of KNO_3 solidifies at − 2°·7
„ „ $NaNO_3$ „ −17·5
„ „ equiv. mixture „ − 7 to −17°.

Hence it appears that the presence of the nitrate of sodium lowers the temperature at which the cryohydrate of the nitrate

of potassium is formed, while the temperature of final solidification is virtually as low as when the nitrate of sodium was alone present.

§ 111. *Mixed Nitrates of Potassium and Sodium as Cryogen.*—The powdered nitrates being mixed in the same proportion as in § 110, namely 11·22 grms. of KNO_3 and 9·44 grms. of $NaNO_3$, and stirred with about 80 grains of crushed ice, gave a temperature of −16°·8. This is clearly again due to the more powerful cryogen $NaNO_3$, which (§ 75) gave −16°·5.

§ 112. *Mixed Chlorides of Potassium and Sodium as Cryohydrate and Cryogen.*—Taking the salts in monomolecular ratio, namely of

KCl taking 18·625
NaCl „ 14·625

dissolving in water and allowing it to stand until crystallization just began, a solution was obtained which solidified completely at −21° C. On mixing the mixture of the same salts in the same proportion with crushed ice, the resulting temperature was −21°·8. The temperatures in both cases are evidently governed by the action of the NaCl; for

The cryohydrate of	KCl	solidifies at	−11°·4
„ „	NaCl	„	−22
„ „	equiv. mixture	„	−21
Temperature of	KCl	as cryogen	−10·5
„	NaCl	„	−22
„	equiv. mixture	„	−21

There is so much difficulty attending the accurate separation of sodium and potassium that no method of analysis of them with which I am acquainted is free from the possible error of 2 or 3 per cent. upon the quantity. Accordingly, for the quantitative study of the mixed cryohydrates or cryohydrate of the mixed salts, the following two simple ones were chosen.

§ 113. *Mixed Chlorides of Potassium and Ammonium as Cryohydrates and Cryogens.*

Of NH_4Cl were taken 13·375 grms.
„ KCl „ 18·625 „

These were dissolved, mixed, and allowed to evaporate till crystallization just began. On cooling, solidification did not begin till −16°·5 or −17°. The temperature remained for a long time at −17°; and when it had reached −18°·8 the

whole mass was solid. Two analyses of the remelted last crop of cryohydrate were made. The solution was weighed into a covered Bohemian-glass basin, evaporated at 100° C. to dryness, kept *in vacuo* over sulphuric acid, weighed, gently ignited, and reweighed.

	grms.		grm.		grm.
(*a*)	4·035	of solution gave	0·9505	of total residue and	0·4890 KCl
(*b*)	5·817	„	1·3725	„ „	0·7005 KCl

So that the percentage compositions were :—

	a.	*b*.	Mean.
KCl . .	12·12	12·04	12·08
NH_4Cl .	11·43	11·55	11·49
H_2O .	76·45	76·41	76·43

The molecular ratios are accordingly

$$KCl = 0{\cdot}1608,\ NH_4Cl = 0{\cdot}2148,\ \text{and}\ H_2O = 4{\cdot}246,$$

or

$$KCl + 1{\cdot}33\,NH_4Cl + 26{\cdot}4\,H_2O,$$

or

$$3\,KCl + 4\,NH_4Cl + 79{\cdot}2\,H_2O.$$

Since the water-worth of NH_4Cl is 12·4 and that of KCl is 16·61 (§ 88), we cannot look upon the compound body as a mixture of the two cryohydrates; but we may perhaps regard it as consisting of seven molecules of the cryohydrate of chloride of ammonium in which three molecules of ammonium are replaced by potassium.

The possible precision in the analysis of the mixed chlorides of potassium and ammonium induced me to extend the examination to the intermediate crops of cryohydrates. Accordingly, the dry salts being mixed as before in equivalent ratio, dissolved, concentrated and cooled, five successive crops of cryohydrate were collected as soon as the temperature had sunk to −16°·5, the last being the mother-liquor.

	(1)	(2)	(3)	(4)	(5	(6)
Solution.....	6·6090	5·8765	4·0540	6·8210	6·4720	5·0750
Total residue ..	1·4810	1·3445	0·9375	1·5720	1·4960	1·2145
KCl	·7870	0·6760	0·4630	0·7815	0·7410	0·5890

Therefore

KCl:	11·90	11·50	11·54	11·45	11·44	11·60
NH_4Cl	10·50	11·37	11·58	11·59	11·67	12·32
H_2O	77·60	77·23	76·88	76·96	76·89	76·08

Hence it appears that the composition of the successive crops of cryohydrate is nearly unchanged. The later the crop, the poorer is it in water and potassium and the richer in ammonium. And the increase in the ammonium is greater than the decrease in the potassium. The same ratio of the same chlorides, when used as a cryogen, gave $-18°$. Accordingly

The cryohydrate of KCl solidifies at $-11°{\cdot}4$.
„ „ NH_4Cl „ -15
„ „ equiv. mixture „ -17

and

As a cryogen KCl gives $-10°{\cdot}5$
„ NH_4Cl „ -16
„ equiv. mixture „ -18

§ 114. *Mixed Nitrates of Barium and Strontium as Cryohydrates and Cryogens.*

7·05 grms. of $Sr\,2NO_3$,

and

8·70 grms. of $Ba\,2NO_3$

were dissolved, mixed, and allowed to evaporate to incipient crystallization. At $-1°{\cdot}2$ a cryohydrate began to form; and the whole was solid at $-4°{\cdot}3$. Employed as a cryogen, the same mixture of salts gave $-5°{\cdot}8$. We have therefore

The cryohydrate of $Sr\,2NO_3$ solidifies at . $-6°$
„ „ $Br\,2NO_3$ „ . $-0°{\cdot}8$
„ „ equiv. mixture solidifies at $-4°{\cdot}3$

and

As a cryogen $Sr\,2NO_3$ gives . . . $-6°$
„ $Ba\,2NO_3$ „ . . . $-0°{\cdot}9$
„ equiv. mixture gives . $-5°{\cdot}8$

§ 115. *Mixed Chlorides of Barium and Strontium as Cryohydrates and Cryogens.*

6·933 grms. of $BaCl_2$

and

5·283 grms. of $SrCl_2$,

both salts having been gently ignited, were dissolved, mixed, and evaporated to saturation. On cooling, a large quantity of transparent salt fell out above 0°. At about $-10°$ a cryohy-

drate began to form, and the whole was nearly solid at $-13°{\cdot}5$ to $-14°$. A small portion, however, remained liquid to $-18°$.

Mixed with snow, the above salts in the above proportion lowers the temperature to $-16°{\cdot}7$. Comparing as before,

The cryohydrate of $SrCl_2$ solidifies at . . $-17°$
„ „ $BaCl_2$ „ . . -8
„ „ equiv. mixture solidifies at -18

and

As a cryogen, $SrCl_2$ gives . . . $-17°$
„ $BaCl_2$ „ . . . $-7{\cdot}2$
„ equiv. mixture gives $-16{\cdot}7$

As it is almost impossible to separate barium and strontium with very great precision, and as it was highly desirable to compare the relative quantities in the cryohydrate in at least one other case besides that of § 113, I chose in the right place the—

§ 116. *Mixed Sulphates of Sodium and Ammonium as Cryohydrates and Cryogens.*

$6{\cdot}6$ grms. of $(NH_4)_2SO_4$

and

$7{\cdot}1$ grms. of Na_2SO_4

were dissolved, mixed, and allowed to evaporate to saturation. On cooling to 0°, acicular crystals were deposited (of sulphate of sodium). At $-4°{\cdot}5$ a cryohydrate began to form; the whole was solid and dry at $-7°$. On analysis, by evaporation to dryness and subsequent strong heating, the portion last to solidify was found in two specimens to have the following composition :—

	a.	*b.*	Mean.
$(NH_4)_2SO_4$.	12·23	12·25	12·24
Na_2SO_4 . .	4·82	4·86	4·84
H_2O . . .	82·95	82·89	82·92

The molecular ratios are accordingly

Na_2SO_4 1
$(NH_4)_2SO_4$ . . . . 2·72
H_2O . . . . . 135·2

or nearly

$$4\,Na_2SO_4 + 11(NH_4)_2SO_4 + 541\,H_2O.$$

As (§ 88) the water-worth of Na_2SO_4 is 165·6, and that of $(NH_4)_2SO_4$ is 10·2, this cryohydrate can neither be regarded as a substitutive cryohydrate like that suggested in § 113 for the cryohydrate of the chlorides of potassium and ammonium, nor as a simply additive cryohydrate; for the joint water-worth is less than that of the ammonium salt alone. The double sulphate of sodium and ammonium is formed; and this has the specific water-worth of 135·2 or (taking the higher molecule) of 541.

That the two salts are not independent of one another, appears from their joint action as a cryogen; for mixed in the above equivalent ratio and stirred with snow, they give −16°. Comparing the joint with the separate effects,

The cryohydrate of $(NH_4)_2SO_4$ solidifies at		−17°
„ „	$NaSO_4$ „	− 0·7
„ „	equiv. mixture solidifies at	− 7

and

As a cryogen, $(NH_4)_2SO_4$ gives .	−17°·5
„ Na_2SO_4 „ .	− 0·7
„ equiv. mixture gives	−16

It is manifest that the doubling of the salt is not taking place during the solution of its two constituents when their mixture is a cryogen, but that it takes place when from solution they unite together in partnership with water as a cryohydrate.

§ 117. *Variation of both Constituents* (AX + BY).—The fascinating hypothesis of Berthollet that double decomposition always partially ensues when two such salts as AX and BY are mixed, even when no removal from the chemical field takes place of any of the possible new bodies resulting from the recombination, may be critically approached from the side of the cryohydrates with great profit. Let me put the question in two concrete forms, and indeed in two of the forms which I immediately propose to examine experimentally.

Is a solution consisting of

202 grms. of KNO_3 and 142 grms. of Na_2SO_4

dissolved in water, identical with a solution consisting of

170 grms. of $NaNO_3$ and 174 of K_2SO_4

dissolved in the same amount of water?

If they are identical, does any one of the salts KNO_3, $NaNO_3$, K_2SO_4, Na_2SO_4 exist as such in either solution?

§ 118. *Comparison between a mixture of* $2NaNO_3$ *and* K_2SO_4 *and a mixture of* $2KNO_3$ *and* Na_2SO_4 *as Cryohydrates and Cryogens.*

33·666 grms. of KNO_3

and

23·666 grms. of Na_2SO_4,

both anhydrous, were mixed, dissolved, and evaporated to saturation. This gave solution (1). Again,

28·333 grms. of $NaNO_3$

and

29 grms. of K_2SO_4

were treated in the same way. This gave solution (2). On cooling (1) and (2), they showed the same behaviour throughout and solidified to dryness at $-5°$. And accordingly there is so far nothing in their behaviour to disprove their identity. But this does not show that partial double decomposition has ensued in both cases to produce in each mixture a portion of the original synthetical constituents of the other. On the contrary, a comparison of this experiment with those above discussed (of the form AX + BX) goes very far to prove, not that there are four salts in each of the solutions 1 and 2, but that there is none of the original salts in either. For it has appeared that when AX and BX are mixed in solution, the temperature of final solidification is in no case sensibly above the temperature required for the solidification of that constituent whose solidification takes place at the lowest temperature. Now, if in solution (1) or (2) there were nitrate of sodium present, whether original or derived, the final solidification would not take place above $-17°$ instead of $-5°$ as found. The absence of nitrate of sodium argues forcibly for the absence of each of the other single salts. The most rational formula for such a mixture is the most empirical one possible. As we cannot intertwine the symbols into a monogram in three dimensions, I arrange them alphabetically, and denote either of the

solutions 1 or 2 by $H_{2n}KN_2NaO_{n+10}S$. I suppose the time will come when it will be held as illogical to consider that KNO_3 exists in a solution of nitre as it would be to regard a circle as a straight line which has been bent round.

§ 119. The same salts as in § 118 were now taken, but not in equivalent quantity; namely

	grms.		grms.
For solution A there were	66 of Na_2SO_4	and	87·72 of KNO_3,
„ B „	91 „ K_2SO_4	„	85 „ $NaNO_3$.

The salts, as before, were mixed, dissolved, evaporated to saturation, and cooled. The solutions being saturated at $+12°$, were first cooled in ice for an hour. During this, two kinds of crystals separated from each in sensible quantity. On further cooling, the temperature became and remained constant at $-5°$ up to solidification. The last liquid portions of A and B having been removed to separate vessels before final solidification, were examined as far as their proportion of sulphuric acid is concerned.

The mother-liquor of A showed in

2·277 grms.
·4205 grm. of ignited residue,
which gave ·2510 of $BaSO_4$,

showing ·0857 or 20·3 per cent. of SO_3 in residue.

The mother-liquor of B showed in

2·434 grms.
·4320 grm. of residue,
which gave ·2390 „ of $BaSO_4$,

showing ·082 or 18·8 per cent. of SO_3 in residue.

§ 120. *Sulphate of Potassium and Choride of Sodium as a Cryohydrate.*—The behaviour of the mixture of these salts also points to the non-existence of either.

8·6 grms. of K_2SO_4,
5·85 „ NaCl
$(=K_2SO_4+2NaCl)$

were dissolved, mixed, concentrated to saturation, and cooled. At first granular crystals fell out. A cryohydrate began to

form at $-6°$. The whole was dry at $-12°{\cdot}5$, whereas if NaCl had been present it would have required $-22°$. A mixture in the ratio $K_2SO_4 + NaCl$ behaved in a similar way, but was dry at $-10°$ C.

§ 121. *Sulphate of Potassium and Chloride of Ammonium as a Cryohydrate.*—Similarly to § 120, a mixture in equivalent proportions of K_2SO_4 and NH_4Cl became quite dry at $-12°$. The salt NH_4Cl alone requires $-15°$.

§ 122. In the subjoined Table the results in regard to mixtures of salts as cryohydrates and cryogens are compared with the behaviour of their constituents in each capacity.

TABLE XV. Cryohydrates and Cryogens of equivalent mixtures of two salts.

Mixed salts.		Temperature of solidification of each constituent as cryohydrate.		Temperature of final solidification of mixture as cryohydrate.	Temperature as cryogen of mixture.
(*a*)	(*b*)	(*a*)	(*b*)	(*a*+*b*)	(*a*+*b*)
(1) KNO_3	$+NaNO_3$...	− 2·6	−17·5	−17	−16·8
(2) KCl	+NaCl.....	−11·4	−22·0	−21	−21·8
(3) KCl	$+NH_4Cl$...	−11·4	−15·0	−17	−18
(4) $Ba2NO_3$	$+Sr2NO_3$..	− 0·8	− 6·0	− 4·3	− 5·8
(5) $BaCl_2$	$+SrCl_2$.....	− 8·0	−17·0	−18	−16·7
(6) $(NH_4)_2SO_4$	$+Na_2SO_4$...	−17·0	− 0·7	− 7	−16
(7) $2KNO_3$	$+Na_2SO_4$...	− 2·6	− 0·7	− 5	
(8) $2NaNO_3$	$+K_2SO_4$ ...	−17·5	− 1·2	− 5	
(9) K_2SO_4	+2NaCl ...	− 1·2	−22·0	−12·5	

This Table furnishes examples of the three typical kinds of relationship between the constituent salts and the mixture of them; namely,

(*a*) In (1), (2), (4), (5) there appears to be no relationship between the salts. Thermally, the mixture may be considered as a mean. The salt of lower solidifying temperature prevents the solidification of the cryohydrate of its associate. The latter in its turn prevents the extreme cold being quite reached proper to the former when alone. In these cases the mixture, when used as a cryogen, gives a temperature a little above that of its more deeply depressive constituent. When jointly forming a cryohydrate, the complete solidification takes place at a slightly

higher temperature than when the more strongly temperature-depressing constituent is alone. The variations from this may not be beyond the limit of observational error.

(*b*) In (3) and (7) double salts must be formed whose cryohydrates demand a lower temperature for solidification than does either of their constituents.

(*c*) Finally, in (8) and (9) the temperature of complete solidification is far above the solidifying temperature of that constituent whose solidifying temperature as a cryohydrate is lowest, where again (in 9) probably a double salt is formed, having, if our analogy hold, a greater water-worth than NaCl and a lesser one than K_2SO_4.

Very remarkable is (6). Prone as the sulphates are to form double salts, we might indeed expect, as we find, a specific temperature for the cryohydrate. The difference of temperature of $a+b$ (6) when used as a cryogen ($-16°$ C.) and when solidifying as a cryohydrate ($-7°$), a difference of 9° C., has at present its only counterpart in iodide of sodium (§§ 65, 68, 69), which as a cryogen has the temperature $-26°{\cdot}5$, as a cryohydrate $-15°$, a difference of $11°{\cdot}5$. Some chemists may not be unprepared for the suggestion that iodide of sodium may be in solution a double salt. To a few general considerations bearing on this and kindred points I may have to return subsequently. Meanwhile the general conclusion to be drawn from the above experiments is probably this. Nitrates of the alkalies and alkaline earths act together, but not in union (no double salts); chlorides may act in union with one another or with sulphates. Sulphates may act together or with chlorides or even with nitrates. The agreement of the composition of the several crops of cryohydrates of (3) (§ 113), which points to the relation of almost exactly $3KCl+4NH_4Cl$, shows that in the society of solid water these chlorides have mutual equivalents, which, if not in simple relation to their so-called atomic weights, are yet equally definite and constant.

I have again to acknowledge my indebtedness to Mr. R. Cowper, who has been good enough to give me great assistance in the above experiments.

II. *On the Polarization of Electrodes in Water free from Air.* *By* J. A. Fleming, *B.Sc.* (*Lond.*), *F.C.S.*, *Science Master in Cheltenham College.*

In the 'Electrical News' for September 2, 1875, I published a short paper, previously read at the Meeting of the Bri tish Association at Bristol, entitled "The Decomposition of an Electrolyte by Magneto-electric Induction." In it experiments were described showing that when an electrolyte (viz. dilute sulphuric acid) flows in a very strong magnetic field, the electromotive force generated by its motion effects the electrolysis of the liquid, such electrolysis being held to be proved by the subsequent polarization of the electrodes. No actual liberation of gases was observed, since the electromotive force brought into play was insufficient to effect free decomposition. At the time it was read Professor H. A. Rowland raised certain doubts as to the correctness of the conclusions drawn; and his remarks were published, appended to my paper, in the 'Electrical News.' As these objections would, if correct, have deprived the experiments entirely of any little interest they might otherwise have had attaching to them, it was obviously necessary to examine them carefully.

Professor Rowland's remarks amounted practically to saying that he thought the electrolyte was not really decomposed, but that the polarization observed was in some way or other due to the presence of dissolved air, and that in air-free liquid the effect would not have been observed, at any rate with the electromotive force (about $\frac{1}{800}$ of a Daniell's cell) which came into play.

To meet these doubts two very definite questions have to be examined.

(i) In air-free water, can platinum electrodes be polarized by very small electromotive forces to the same degree and with the same facility as in ordinary aerated water?

(ii) Is this very feeble polarization really a decomposition of the electrolyte?

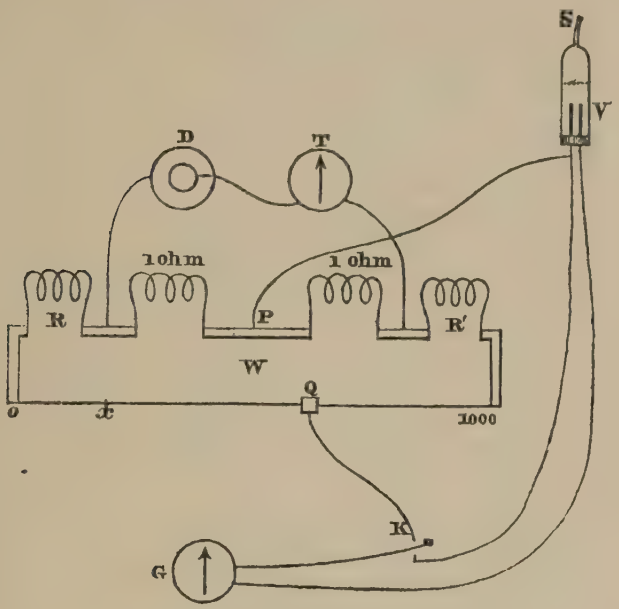
If the following facts are held to give an affirmative answer to both the above questions, the objections raised are invalid and may be dismissed.

To test the first point, it was necessary to compare the effect of a small known electromotive force acting through platinum electrodes, first in air free, next in aerated acidulated water, under identical conditions. In the former experiments the electromotive force was generated *in* the liquid by its motion; for my present purpose it was sufficient to act on it by an *external* electromotive force of measurable amount, since it is obvious the results hold good no matter how it is produced. The arrangement consisted of the following parts.

The decomposing cell or voltameter was a glass tube 30 centims. long, $2\frac{1}{4}$ centims. wide, stopped at one end by an india-rubber stopper, through which passed two platinum wires having welded to them on the interior platinum plates 8 centims. long, 2 centims. wide, placed so as to lie against the walls of the tube. The other end of the tube was connected by a narrow tube with the Sprengel pump. The platinum plates having been rendered chemically clean, the tube was three parts filled with dilute sulphuric acid, which had been previously boiled for six hours so as to expel some of the dissolved air. A vacuum was then made in the voltameter; and the apparatus remained untouched for five days, the pumping being carried on at intervals and continued during the experiments.

To obtain a small electromotive force a well-known method was made use of. A Wheatstone's bridge had its branches filled up with previously measured resistances, and the other connexions made as in the figure (p. 17). Between the points P and Q any small difference of potentials can be produced whose value is known when the distance x Q of the block from the point of equilibrium x is known. The galvanometer employed was a very sensitive mirror-galvanometer, with short needle and a long suspending fibre. The image of a fine wire across the slit was reflected on to a scale in the usual way, and the image viewed through a telescope placed behind the galvanometer. By this means it was found possible to detect and read deflections of the needle amounting only to $\frac{1}{16}$ of a degree with great ease. With this delicate arrangement it was a matter of great difficulty to get the platinum plates perfectly neutral. The last traces of polarization from previous experi-

ments subsided with extreme slowness. The following operations were then performed :—



W. Wheatstone's bridge.
D. Daniell's cell.
T. Tangent-galvanometer.
V. Voltameter.
G. Mirror-galvanoscope.
K. Key.
S. Tube to Sprengel pump.

(i) The electrodes were made perfectly neutral.

(ii) The galvanometer excluded from the circuit, and a direct current sent through the decomposing-cell for one minute.

(iii) The polarization measured by the swing made by the galvanometer-needle when the electrodes were suddenly connected with it.

(iv) The swing or excursion made by the needle when the same direct current was started through the cell and galvanometer in one circuit, previously bringing the platinum plates to a neutral condition.

The first column in the subjoined Table gives the bridge-reading, the second the electromotive force which this is equivalent to in absolute units (C. G. S.), the third the swing of the needle with the direct current (charging), fourth the same with the polarization current (discharge).

TABLE I.—Polarization in Acidulated Water free from Air and kept *in vacuo*.

Bridge-reading.	Electromotive force.	Excursion of needle in degrees or fractions.	
		Direct current.	Polarization current.
275	12110	° $\frac{1}{3}$ barely.	° $\frac{1}{6}$
280	18165	$\frac{1}{2}$ full.	$\frac{1}{4}$ nearly.
285	24220	$\frac{3}{4}$ nearly.	$\frac{1}{4}$ full.
290	30275	$\frac{3}{4}$	$\frac{1}{2}$ nearly.
300	42385	1	$\frac{1}{2}$
310	54495	$1\frac{1}{2}$	$\frac{1}{2}$
320	66605	2	$\frac{5}{8}$ nearly.
330	78715	$2\frac{1}{4}$	$\frac{5}{8}$
340	90825	...	...
350	102935	3	$\frac{3}{4}$
400	115045	5	1
450	224035	7	$1\frac{3}{4}$
500	284585	10	$2\frac{1}{2}$

Since a Daniell's cell is about 100,000,000 units in electromotive force, the above Table shows that, with the galvanometer employed, the least electromotive force which, acting for one minute under these circumstances on platinum plates of 16·39 centims. surface, would leave a detectable polarization, was about $\frac{1}{8000}$ of a Daniell's cell.

The observations having been repeated several times with the same results, the dilute acid was then removed, and thoroughly aerated by shaking it up with air under pressure, and by bubbling air through it for some time. This aerated water was then returned to the voltameter, all other arrangements remaining the same, and the same observations repeated in this case as in the last. The results are appended.

TABLE II.—Polarization in Acidulated Water thoroughly well aerated.

Bridge-reading.	Electromotive force.	Excursion of needle in degrees or fractions.	
		Direct current.	Polarization current.
275	12110	° ⅛ barely.	° ⅛
280	18165	¼	⅛
285	24220	⅜	¼ barely.
290	30275	½	¼
300	42385	1¼	⅜ barely.
310	54495	1½	½
320	66605	2 barely.	⅝
330	78715	2	¾ barely.
340	90825	...	...
350	102935	3	¾
400	115045	5	1
450	224035	7	1½
500	284585	10	2¾

An examination of these two Tables shows that there is very little difference between them which cannot properly be ascribed to errors in observation. There is *no* difference in the minimum electromotive force which could give in each case a visible polarization with the galvanometer employed. But now there was one very striking difference between the two sets of experiments, not shown in the Tables, viz. the time required after each experiment for the polarization to subside. In the case of the aerated water, the polarization disappears *very much* more quickly when the plates are short, circuited than in the case of the air-free water. With this latter it was most troublesome to get rid of the last traces, even with the smallest polarizing currents. This has been previously noticed and explained by Helmholtz *. It is, however, a point not involved in our present considerations.

A consideration of these observations leads apparently to the conclusion that the presence of air in the water has no effect in creating or assisting the polarization of the electrodes under a

* Phil. Mag. [IV.] vol. xlvii. p. 152, Dr. Helmholtz "On Galvanic Polarization in Liquids free from Gas."

feeble electromotive force (it is difficult to see any reason why it should), although it has a great effect in removing it when once formed. The process called by Helmholtz *electrolytic convection*, and in which dissolved air is essential, is the consequence and not the cause of polarization.

It is not true that it requires any definite electromotive force to begin to polarize electrodes in air-free water; any electromotive force, however small, will do it. Its detection is only a question of a sufficiently delicate galvanometer; and we may therefore say that any electromotive force, however feeble, acting on platinum electrodes, builds up a corresponding amount of polarization equally in air-free as in aerated water. But no liberation of free gas is possible under these circumstances, until the external electromotive force just exceeds the counter-electromotive force of the electrodes when polarized to their fullest extent.

With regard to the second question, whether polarization, however small, means literal chemical decomposition, I am not aware that it has ever been called into questiom. There is abundant evidence to show that it is not a mere physical state of the chemically unaltered electrolyte, but that there is *something* deposited on the electrodes which can only be the products, primary or secondary, of electrolysis. Although a voltameter charged by a weak electromotive force resembles very closely a condenser, yet there is something very different between the state of strain or electrical displacement in a condenser's dielectric and the electrolyte after having had a current passed through it.

That even very feeble polarization does really in every case consist in the deposition of products of an unseen electrolysis in or on the electrodes receives support, in addition to many other facts, from the following :—Platinum plates were placed in the inside of a vertical glass tube, and made to communicate with the outside by wires sealed through the glass. The tube was so arranged that dilute acid could be made to flow down through the tube from a reservoir, without the plates being ever exposed to air. The tube being full of acid, the platinum plates were now polarized feebly. If the acid was allowed to flow out *slowly*, so as to gradually replace the liquid which was between the plates when polarized by other fresh acid, the

plates gave, on discharge, a nearly equal current to that which they would have given if no replacement had been made; but if the liquid was made to rush down *violently* and then stopped, little or no polarization was found, provided the plates had been only slightly polarized. If the plates were defended by strips of cloth laid over them, no such removal was effected by the liquid rushing down. This all seems to indicate that there is something on the plates which can be *wiped off* mechanically. This can only be the products of electrolysis. This experiment has no analogy in a condenser. These and many other facts seem to point out that polarization is in all cases only unseen electrolysis.

In conclusion I cannot but think that the objections raised to the former experiments were groundless, and that, when it is found that a stream of acidulated water flowing down between the poles of a magnet polarizes platinum plates placed in it, we are entitled to call it chemical decomposition, since it would only be necessary to exalt the magnet's power and increase the velocity of flow in order to see, under certain precautions, the liberated gases streaming from the plates.

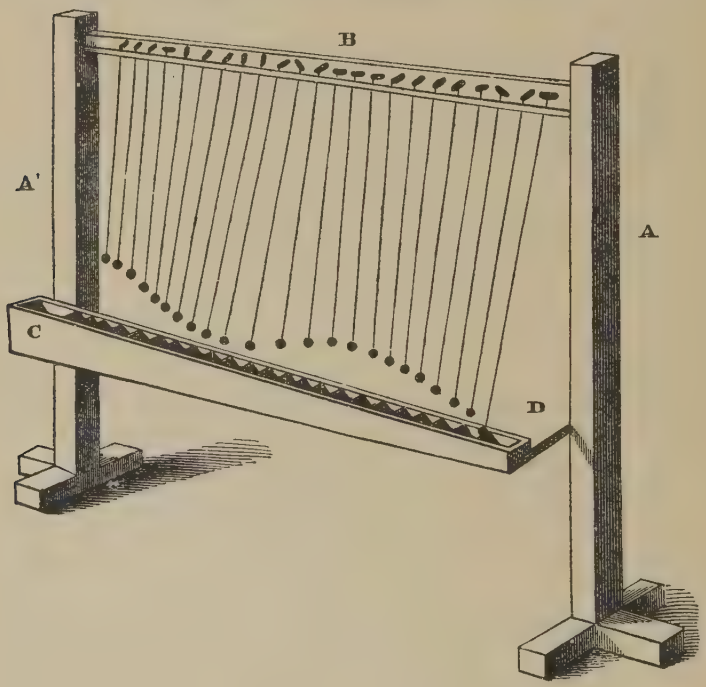
III. *On a new Form of Wave-apparatus suitable for the Lecture-room.* *By* C. J. Woodward, *B.Sc.**

The apparatus about to be described illustrates the motion of the air-particles when a sound-wave is propagated, and also the motion of the æther molecules in a wave of plane-polarized light.

Wave motion consists in the repetition by a number of particles of some prescribed motion which is given to the first of the particles and taken up successively by the others, a certain interval elapsing between the successive motions. If, for example, we have a number of pendulums of equal length hanging from a beam, but their lower ends supported so that they are out of the vertical, we shall find on releasing one of them, say the left-hand end one, it will commence swinging to and fro; by the time the first pendulum has gone over one fourth of its path release the second, and then after equal intervals

the third, fourth, &c., and a wave motion will be produced. If each pendulum was drawn aside in a line at right angles to the beam from which they are suspended, a wave corresponding to a ray of polarized light will be produced; but if each had been drawn aside in the same plane as that of the beam, a wave corresponding to that of a ray of sound would be obtained. We require, then, in order to illustrate these waves, merely a row of pendulums and some arrangement for releasing them in succession.

The apparatus I have used is represented in the figure. A, A



Plane wave produced by placing the pendulums in the compartments of the box C and releasing them in succession by lowering the box. In the figure the last ball is about leaving the box.

are two uprights about 10 feet high, with a crosspiece B fastened firmly to them. At intervals of 3 inches along this crosspiece are inserted violin-pegs, each peg carrying a light string

with a heavy ball of 1 inch diameter attached. Before fastening the strings to the violin-pegs, each string is passed through a small hole in the projecting base of the crosspiece, so that the length of the pendulum is determined by the distance of the ball from the base of the crosspiece. C is a light wooden box deeper at one end than at the other, with a number of compartments corresponding to the number of pendulums. The box C is attached at the ends to two radial arms, one of which, D, is seen in the figure. Cords are also attached to C running over pulleys, by which the box C may be raised and lowered. These cords would confuse the figure if introduced; and their action can be easily realized.

Suppose it be wished to illustrate a plane wave. The box C is raised, and the pendulums are placed one in each compartment so that they are all drawn on one side. By means of the cords the box C is gently lowered, when the pendulums are successively released and the wave formed.

To illustrate the sound-wave, the box C is removed from the radial arms and is hung vertically underneath the crosspiece B; one or two of the pendulums (to the left, say) are removed, and the others placed in the compartments as before; only now each pendulum, instead of being drawn from under the crosspiece, lies still underneath, but to the left of the vertical line let fall from each point of support. On now allowing the box to fall slowly, the pendulums are released successively and a wave of condensation and rarefaction is formed.

In conclusion I should acknowledge the assistance of Mr. H. F. Marshall, of Birmingham, who has rendered great service in simplifying the mechanical arrangements of the apparatus.

Birmingham and Midland Institute,
January 1876.

IV. *On some Problems connected with the Flow of Electricity in a Plane.* *By* OLIVER J. LODGE, *B.Sc.**

The following paper may be regarded as a sort of appendix to a paper by Professor G. C. Foster and myself, entitled "On the Flow of Electricity in a uniform plane Conducting Surface," and published in the Philosophical Magazine for May, June, and December 1875 ([IV.] vol. xlix. pp. 385–400 and 453–471, and vol. l. pp. 475–489), in which the known laws of the flow of electricity in an unlimited plane were deduced from the fundamental idea that the effects of any number of poles could be obtained by simple summation of the effects due to each pole separately, without using any mathematics higher than elementary algebra. Several questions arose in the course of the paper which it was not thought advisable to consider then, but some of which seemed to deserve a separate treatment; these are the subjects I propose to develop in the present communication.

§ 1. Imagine a plane sheet, some portions having infinite conducting-power, other portions consisting of ordinary matter, and again other portions possessing infinite resisting-power. The whole extent of any of the infinitely conducting regions will have a uniform potential; and hence the bounding line between any such region and the ordinary matter of the sheet must be an equipotential line. Further, if one defines a line of flow or stream-line as a line across which no electricity passes, the boundary line between the ordinary matter of the sheet and an infinitely resisting region must be a line of flow, for no electricity can possibly get across it. Such a sheet will therefore contain a certain number of flow-lines and a certain number of equipotential lines. Moreover let the potential of any one of the conducting regions be maintained higher than that of some other one, then in general a uniform flow of electricity will take place throughout the whole of the ordinary matter of the sheet, which will therefore contain additional stream-lines and equipotential lines, whose arrangement will depend on the situations and potentials of the various non-material regions.

Some general properties of the equipotential and stream-

* Read on the 26th of February and the25th of March, 1876.

lines were pointed out in § 35 of the paper referred to. One of these properties is, of course, that the lines of one system cut the lines of the other orthogonally; a more general statement is the following. If a flow-line passes n times through a given point of the sheet, it will form at that point an equiangular pencil whose $2n$ rays meet each other at an angle $\frac{\pi}{n}$; and if no pole exists at the meeting-point it will be a point of no flow, and an equipotential line will also pass n times through the same point, making an equiangular pencil the same in all respects as the former, but turned through an angle of $\frac{\pi}{2n}$, so that its rays bisect the angles of the first pencil. The ordinary orthogonal section is the special case of this when $n=1$. The special case $n=\infty$ is obtained if, in the sheet imagined above, one of the conducting regions touches one of the resisting regions along a line; when this happens, the line separating the two may be regarded indifferently as a stream-line or as an equipotential line.

There are then two ways of making any given line a stream-line—viz. either by arranging the non-conducting regions so that the line shall bound one of them, or else by arranging the conducting regions and their potentials in such a way that none of the flow of electricity shall take place *across* any portion of the given line. Similarly any line may be made an equipotential line, either by making it bound a region of infinite conductivity, or else by adjusting the potentials and positions of these same regions so that no part of the flow shall take place *along* the given line.

Such a sheet as we have imagined can be approximated to by a piece of tinfoil cut to any shape, with any number of holes in it, and having on its surface blocks of clean copper which are connected with a thermo-pile or other means of maintaining constant difference of potential.

§ 2. The conditions of flow in such a sheet, however, are in general unknown. But if infinitely resisting regions are absent, and if the infinitely conducting regions are reduced to mere points of infinite potential, we get the case of an unlimited sheet containing point poles; and in this all the conditions of the flow are completely known for every point of the sheet.

Thus the potential at any point distant r_1, r_2 ... from the poles which emit quantities of electricity q_1, q_2 ... in unit time, and which tend to produce potentials ϕ_1, ϕ_2 ... at unit distance from themselves, is (§ 33 of the former paper)

$$V = \Sigma\phi - \frac{1}{2\pi\kappa\delta}\Sigma q \log r, \quad . \quad . \quad . \quad . \quad . \quad (A)$$

where δ is the thickness and κ the specific conductivity of the sheet; and from this expression stream-line equations and resistance expressions follow.

So, then, the problem of finding the flow conditions in any bounded sheet containing point poles will be solved if we can imitate the electrical boundary conditions in an unlimited sheet by introducing extra point poles into it. These additional poles are called images in the boundary, because they produce the same effect in the given portion of the sheet as the boundaries themselves produced—just as the illumination inside a mirror-walled room containing candles would be imitated in unlimited space by placing extra candles at all the points occupied by the images of the original candles in the mirrors.

Images in rectilinear boundaries.

§ 3. Now let it be required to cause a given *straight* line in an infinite sheet of tinfoil to be a stream-line. All that is necessary is to arrange all the blocks of copper in the sheet symmetrically with respect to this line; that is to say, they must either be placed symmetrically upon the line, or they must be placed in pairs one on each side of it and at equal distances from it. It is usual to express this fact in the inverse way thus:—The image of a pole in a straight flow-line is a pole of the same size, shape, and strength, and situated at an equal distance on the other side of the line so as to be opposite to the first pole.

Again, in order to make a given straight line into an equipotential line, the blocks must be arranged skew-symmetrically with respect to the line—that is to say, in pairs one on each side of it and at equal distances from it, but the sign of one of the constituents of each pair must be opposite to that of the other. This fact is expressed thus:—The image of a pole in a straight equipotential line is a pole of the same size, shape, and

numerical strength, but of opposite sign, and situated at an equal distance on the other side of the line.

Hence, if we have given a sheet of tinfoil bounded by a straight edge (*i. e.* by a straight flow-line) and with any distribution of poles in it whatever, and we wish to find the distribution of poles which would make that straight line a flow-line in the unlimited sheet, we have only to regard the line as a plane mirror whose silvered face is turned towards the sheet, and the optical images of the several poles will give the distribution required. The distribution of poles will be obtained in the same way if the boundary is a straight band of copper (*i. e.* an equipotential line); but in this case the sign of every image must be reversed.

§ 4. Now take a sheet bounded by two straight flow-lines intersecting one another at any angle θ: every pole in such a sheet will be reflected backwards and forwards between the two edges according to optical laws; and hence it should have a finite series of images lying on a circle and agreeing with those in the kaleidoscope, the reflection coming to an end as soon as a couple of images fall in the space which is behind both mirrors. But here arises a difficulty. When θ is a submultiple of π, the last couple of images coincide and the whole set is symmetrical with respect to both the straight lines, as is required. But if θ is not a submultiple of π, all that happens in the case of the kaleidoscope is that the last two images separate, the apparent number of images being simply increased by 1. But now the images are not arranged symmetrically with respect to *both* the straight lines, and hence they cannot both be flow-lines. In order to obtain symmetry, it is necessary to continue the reflecting process as if the back of the mirrors were silvered as well as the front; and in that case, of course, the number of images becomes infinite. But then some of these infinite images will fall inside the angle θ (that is, will come into the sheet itself), which will be inconsistent with the given distribution of poles in the sheet. Hence it appears to be impossible for the uniform infinite sheet to contain two straight flow-lines which enclose any angle but a submultiple of π, unless the poles are put infinitely close together, forming a complete circular ring whose centre is at the intersection of

the two lines; and in this case *every* straight line drawn in the sheet from this centre is a flow-line.

Another way of expressing the facts is to say that both sides of *every* flow-line are to be regarded as mirrors, and its images as always infinite in number though often coincident with one another, and that the problem of reducing the bounded case to that of the infinite sheet becomes impossible whenever the images reflected back into the sheet itself do not coincide both in sign and position with the images already there. Similar statements are true of the images in a pair of intersecting equipotential lines.

Another distinction between optical and electrical reflection is, that when two optical images coincide their light-emitting powers are added, but, in the electrical case, coincidence of one image with another does not increase its strength. These differences appear to forbid our imagining that there is any physical meaning in electrical reflection at boundaries analogous to the physical reflection of the waves of light in a mirror.

§ 5. Consider now the images of a point inside a polygon of n sides. We have seen that, without silvering both faces of the boundaries and thereby introducing an unconscionable number of images, some of them *real*, we can only treat angles that are submultiples of π by the method of images. Hence obtuse angles less than π are not allowable. This condition at once excludes all polygons of more than four sides; for as the largest interior angle of a polygon of n sides cannot be less than $\frac{n-2}{n}\pi$, and as it must be less than or equal to $\frac{\pi}{2}$, it is necessary that n shall be equal to or less than 4. And if $n=4$, the polygon must be equiangular, that is, must be a rectangle. If $n=3$, the triangles whose angles are submultiples of π are the equiangular, the isosceles right angled, and the one whose angles are 90°, 60°, and 30°. The pseudo-triangle whose angles are 90°, 90°, and 0° is also a possible case, and is treated below as a special case of the circular sector.

I have not mentioned the case when π itself is one of the angles of a polygon, because this merely reduces the polygon to one of $n-1$ sides; but there is the case of the equiangular

polygon with all its angles π, viz. the circle, about which a little shall be said later.

The images of a point in a rectangle occur in groups of four surrounding the vertices of rectangles whose linear dimensions are twice those of the original one, and which cover all the plane.

The images of a point in an equilateral triangle occur in groups of six surrounding the vertices of triangles $\sqrt{3}$ times the linear dimensions of the original one, and covering all the plane.

Application of images to certain cases of bounded plates.

§ 6. Now although the potential of any point is really determined by (A), § 2, as soon as we know the positions of all the images in the sheet, the expression is not in a practicable form; and it would not in the majority of cases be readily possible to bring it to such a form. The way to proceed in such cases is to consider what is required of the potential, and then to write down a function of $x+iy$,

$$W \equiv V + Ui,$$

such that the real part satisfies all the conditions required of the potential function, viz. to remain together with its derivatives continuous and finite all over the sheet except at the poles and their images, where it is to become infinite like $q \log r$, to fulfil certain given conditions at the boundary, and to satisfy the equation

$$\frac{d^2V}{dx^2} + \frac{d^2V}{d^2} = 0.$$

This being done, $V = \text{const.}$ will represent the equipotential lines, and $U = \text{const.}$ the stream-lines, and the components $\frac{dV}{dx}, \frac{dV}{dy}$ of the flow at any point can be obtained. In this way Dr. E. Jochmann * has expressed all the conditions of the flow in a *rectangle*, bounded either by stream-lines or by equipotential lines, or by both.

* "Ueber einige Aufgaben, welche die Theorie des logarithmischen Potentials und den Durchgang eines constanten elektrischen Stroms durch eine Ebene betreffen," von Dr. E. Jochmann in Berlin. Schlömilch, *Zeitschrift für Mathematik*, 1865, p. 48.

§ 7. But though the potential expression (A) is often of impracticable form, the expression for the resistance of a conductor, which follows from it, is simpler, and admits of being reduced to a useful form with much ease in many cases. Expressions so obtained may serve to verify the results of more abstruse and general processes; but the principal reason for entering into the subject is that the expressions themselves and several of the continued products which lead to them seem to be of some little mathematical interest.

Resistance of some rectilinear figures to the current flowing between two small circular electrodes.

§ 8. Let us first remind ourselves how the general resistance-expression is obtained. Given an infinite sheet with any number k of *equal* sources $A_1, A_2, \ldots A_k$ and the same number of equal sinks $B_1, B_2, \ldots B_k$ in it, the resistance between the two equipotential lines which pass through any two fixed points P and Q is given by Ohm's law as

$$R_{PQ} = \frac{V_P - V_Q}{kq},$$

where V_P stands for the actual potential at the point P, and kq stands for the whole strength of current flowing in the sheet—that is to say, for the quantity of electricity emitted by each source per second, multiplied by the number of sources. Now (A) gives as the potential at any point P

$$V_P = -\frac{q}{2\pi\kappa\delta}\log\frac{A_1P \,.\, A_2P \ldots}{B_1P \,.\, B_2P \ldots}, \quad \ldots\ldots\ldots \quad (A)'$$

hence

$$R_{PQ} = \frac{1}{2k\pi\kappa\delta}\log\left\{\frac{A_1Q \,.\, A_2Q \ldots}{B_1Q \,.\, B_2Q \ldots} \,.\, \frac{B_1P \,.\, B_2P \ldots}{A_1P \,.\, A_2P \ldots}\right\}. \quad \ldots \quad (B)$$

And these expressions are perfectly general; for unequal poles may be regarded as aggregations of equal ones, and the number of sinks *must always* be equal to the number of sources, although some of them may often be at infinity.

Now we know that the equipotential lines of high potential break up into k portions which ultimately become little circles, one surrounding each source. Similarly the lines of low potential surround the sinks. Take the point P on the circumference of one of these little circles (radius ρ_1), that surround-

ing the source A say (omitting its suffix); and take the point Q on a circle (radius ρ_2) surrounding the sink B. Then the resistance between the two small circular electrodes A and B is k times as much as that offered by the sheet to the $2k$ poles, or

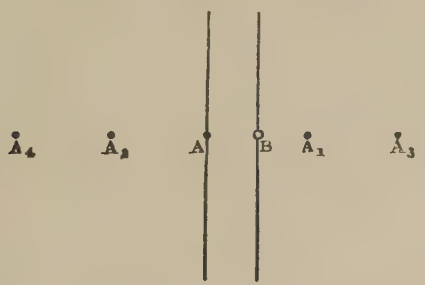
$$R_{AB} = \frac{1}{2\pi\kappa\delta} \log \left\{ \frac{AB \,.\, A_1B \,.\, A_2B \ldots}{\rho_1 \,.\, A_1A \,.\, A_2A \ldots} \,.\, \frac{BA \,.\, B_1A \,.\, B_2A \ldots}{\rho_2 \,.\, B_1B \,.\, B_2B \ldots} \right\}, \quad (\alpha)$$

where the higher powers of ρ_1 and ρ_2 are neglected. Since they are both small there is no necessity to distinguish them, and ρ^2 may be written for their product. Moreover in very many cases the sources and sinks will be similarly arranged; so that the two fractions which are multiplied together inside the brackets of (α) are equal to one another, and we may then use the simplified expression

$$R_{AB} = \frac{1}{\pi\kappa\delta} \log \left(\frac{AB \,.\, A_1B \,.\, A_2B \ldots}{\rho \,.\, A_1A \,.\, A_2A \ldots} \right). \quad . \quad . \quad (\beta)$$

§ 9. Before proceeding to apply the image theory and this expression to the general case of a two-sided figure, it will be well to consider a special case or two,—and first the very simple case of a parallel-sided strip of breadth s, with the two poles, A and B, one on each side of the strip and opposite to one another (fig. 1).

Fig. 1.



A will be reflected in the opposite side, its image A_1 being at a distance s from that side and from B; then A_1 will be reflected, its image A_2 being $2s$ distant from A and $3s$ from B; then A_2 will be reflected, and so on. The images of B will evidently be similarly arranged to those of A *mutatis mutandis*:

so we may use the second of the resistance-formulæ

$$R=\frac{2}{\pi\kappa\delta}\log\frac{AB\,.\,A_1B\ldots}{\rho\,.\,A_1A\ldots},$$

doubling it because the poles are only halfway on the sheet (see below, § 22). Now

$$AB=A_1B=s, \qquad A_1A=A_2A=2s,$$
$$A_2B=A_3B=3s, \qquad A_3A=A_4A=4s,$$
$$A_4B=A_5B=5s, \qquad \ldots\ldots$$
$$\ldots\ldots$$

Hence the above product becomes

$$\frac{s}{\rho}\cdot\frac{1.3.3.5.5.7\ldots}{2.2.4.4.6.6\ldots},$$

which equals $\frac{s}{\rho}\cdot\frac{2}{\pi}$.

Therefore

$$R=\frac{2}{\pi\kappa\delta}\log\frac{2s}{\pi\rho}. \qquad \ldots\ldots \quad (1)$$

§ 10. One more special case of the infinite strip I will take, because a constantly occurring product occurs here in its simplest form. Let the two poles be both on the same side of the strip and at a distance c from one another. The images of A are just as before, and the product $\frac{AB}{\rho}\cdot\frac{A_1B}{A_1A}\cdot\frac{A_2B}{A_2A}\ldots$ equals

$$\left\{\frac{c^2}{\rho^2}\cdot\frac{2^2s^2+c^2}{2^2s^2}\cdot\frac{2^2s^2+c^2}{2^2s^2}\cdot\frac{4^2s^2+c^2}{4^2s^2}\cdot\frac{4^2s^2+c^2}{4^2s^2}\cdots\right\}^{\frac{1}{2}}$$
$$=\frac{c}{\rho}\left(1+\frac{c^2}{2^2s^2}\right)\left(1+\frac{c^2}{4^2s^2}\right)\left(1+\frac{c^2}{6^2s^2}\right)\cdots$$
$$=\frac{c}{\rho}\cdot\frac{\sinh\frac{\pi c}{2s}}{\frac{\pi c}{2s}}\ *.$$

* Here and elsewhere sinh x may be considered merely an abbreviation for $\frac{e^x-e^{-x}}{2}$, or as equal to $\frac{1}{i}\sin ix$. Similarly

$$\cosh x=\frac{e^x+e^{-x}}{2}, \text{ or } =\cos ix,$$

and

$$\tanh x=\frac{e^x-e^{-x}}{e^x+e^{-x}}=\frac{1}{i}\tan ix,$$

Therefore

$$R=\frac{2}{\pi\kappa\delta}\log\left(\frac{2s}{\pi\rho}\sinh\frac{\pi c}{2s}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Similarly, if we had taken the poles one on each side of the strip, but, instead of opposite each other as at first, at a distance c from one another measured parallel to the sides of the strip, we should have obtained

$$R=\frac{2}{\pi\kappa\delta}\log\left(\frac{2s}{\pi\rho}\cosh\frac{\pi c}{2s}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If s be made infinite, (2) becomes $\frac{2}{\pi\kappa\delta}\log\frac{c}{\rho}$, which is the correct expression for the case of two poles on the edge of half an infinite sheet. If s is small, (2) and (3) become equal; and if $s=\rho$, they reduce to $R=\frac{c}{\kappa\rho\delta}$ (neglecting the small term $-\frac{2}{\pi\kappa\delta}\log\pi$), which is right for the resistance of a wire or thin strip of sectional area $\rho\delta$ and length c. The presence of the term neglected in comparison with a term which has ρ in its denominator, can be accounted for by remembering that the electrodes are not exactly straight bars at a distance c, but quadrants of small circles whose *centres* are distant c from one another.

§ 11. We may also consider one special case of the infinite "wedge" or *irregular* two-sided polygon. Let the two poles be one on each side of the wedge at the same distance r from its angle O, and call this angle $\theta=\frac{\pi}{n}$ (n integer). The images of A will lie on a circle with centre O (fig. 2), as in the kaleidoscope.

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where $i=\sqrt{-1}$. It is useful to remember that

$$\cosh^2 x-\sinh^2 x=1,$$

that

$$\sinh 0=\tanh 0=\sin 0=0,$$

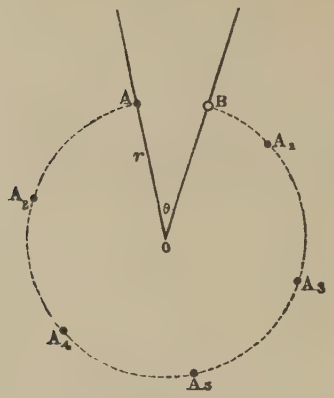
that

$$\cosh 0=\tanh\infty=1,$$

and that

$$\sinh\infty=\cosh\infty=\tfrac{1}{2}e^{\infty}$$

Fig. 2.



Then

$$A\,B = A_1B = 2r\sin\frac{\theta}{2}, \qquad A_1A = A_2A = 2r\sin\frac{2\theta}{2},$$

$$A_2B = A_3B = 2r\sin\frac{3\theta}{2}, \qquad A_3A = A_4A = 2r\sin\frac{4\theta}{2},$$

. . . . . ;

so the product which occurs in (β) equals

$$\frac{2r}{\rho}\cdot\frac{\sin^2\frac{\theta}{2}\sin^2\frac{3\theta}{2}\sin^2\frac{5\theta}{2}\cdots}{\sin^2\frac{2\theta}{2}\sin^2\frac{4\theta}{2}\sin^2\frac{6\theta}{2}\cdots}\begin{cases}\dfrac{\sin^2\frac{n-1}{2}\theta}{\sin^2\frac{n}{2}\theta}\sin\dfrac{n\theta}{2} & \text{when } n \text{ is even,}\\[2ex] \dfrac{\sin^2\frac{n-2}{2}\theta}{\sin^2\frac{n-1}{2}\theta}\sin\dfrac{n\theta}{2} & \text{when } n \text{ is odd.}\end{cases}$$

But we know from Trigonometry that

$$\sin\frac{\pi}{2n}\sin\frac{3\pi}{2n}\cdots\begin{cases}\sin\dfrac{n-1}{2n}\pi\\ \sin\dfrac{n-2}{2n}\pi\end{cases} = 2^{\frac{2}{n-1}},$$

and that

$$\sin\frac{2\pi}{2n}\sin\frac{4\pi}{2n}\cdots\begin{cases}\sin\dfrac{n-2}{2n}\pi\\ \sin\dfrac{n-1}{2n}\pi\end{cases} = 2^{\frac{2}{n-1}}\sqrt{n},$$

the upper termination to be taken when n is even, the lower when n is odd. Hence the above product equals

$$\frac{2r}{\rho}\cdot\frac{1}{n},$$

and

$$\mathrm{R}=\frac{2}{\pi\kappa\delta}\log\frac{2r\theta}{\pi\rho}\ \text{or}\ =\frac{2}{\pi\kappa\delta}\log\frac{2s}{\pi\rho}, \quad . \quad . \quad . \quad (4)$$

if one writes s for the arc subtending θ of the circle whose radius is r.

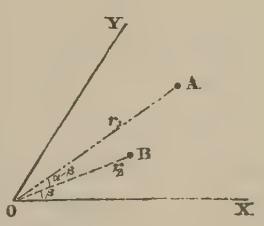
Notice here the close resemblance to (1), becoming identity when $r=\infty$, and also the sort of circular analogy to Wallis's form of $\frac{\pi}{2}$ which one gets by taking arcual instead of linear distances in fig. 2 for the product of (β).

The circle on which all the poles lie is a flow-line by symmetry; and hence the resistance of the sector A O B is twice that of the wedge.

General resistance of a "Wedge," or two-sided polygon, poles any where.

§ 12. If we obtain an expression for the case of two poles A and B, it will be little more than a matter of writing to extend it to any number. Let O X and O Y be the two sides of the wedge, the angle Y O X being $\theta=\frac{\pi}{n}$. Call the distance O A, r_1; and the angle A O X, α (fig. 3); and let (r_2, β) denote the point B. The images of A will lie in pairs on a circle of radius r_1, those of B on a circle of radius r_2; and to find the value of the products which occur in the general expression (α) we may make use of Cotes's (or Demoivre's) property of the circle, which says that, if m points equisect the circumference of a circle of radius r_1, the product of their distances from another point, distant r_2 from the centre of the circle and $\surd(r_1^2-2r_1r_2\cos\phi+r_2^2)$ from the nearest of the m points, will be equal to

Fig. 3.



$$\surd(r_1^{2m}-2r_1^mr_2^m\cos m\phi+r_2^{2m}). \quad . \quad . \quad . \quad . \quad (C)$$

To apply this theorem to the present case we must consider the images of A in two sets:—one set including A itself and all its images whose angular distance from it is some multiple of 2θ; the other set containing all the remaining images, which will alternate with those of the first set, and will like them divide the circle into n equal parts. The product of all the distances of the first set from the point B will be given by (C) if we put $m=n=\frac{\pi}{\theta}$ and $\phi=\alpha-\beta$; the product for the second set will only differ in having $\phi=\alpha+\beta$. From the symmetry of the expression, it follows that the product of the distances of the images of B from the point A will be the same as that of the images of A from the point B. Hence the numerator of (α) is determined. As for the denominator, the product of the distances of the second set of images of A from the point A is

$$2r_1^n \sin n\alpha.$$

The product of the first set appears to be zero, since A itself is one of the set; but remembering that the point to which distances are properly measured is not the actual pole A but a point on the circumference of its small electrode (§ 8), we see that the product becomes

$$r_1^n-(r_1-\rho)^n=nr_1^{n-1}\rho,$$

neglecting high powers of ρ. So the whole product of the A's from A is $2n\rho r_1^{2n-1}\sin n\alpha$; similarly the product of the B's from B will be

$$2n\rho r_2^{2n-1}\sin n\beta.$$

Hence the resistance-expression (α) reduces to

$$\Re=\frac{1}{2\pi\kappa\delta}\log$$

$$\frac{\left(r^{2n}-2r_1^n r_2^n r\cos n(\alpha-\beta)+r_2^{2n}\right)\left(r^{2n}-2r_1^n r_2^n\cos n(\alpha+\beta)+r_2^{2n}\right)}{4n^2\rho^2 r_1^{2n-1}r_2^{2n-1}\sin n\alpha\,.\,\sin n\beta},\quad(5)$$

or, as it is often more convenient to write it,

$$=\frac{1}{2\pi\kappa\delta}\log$$

$$\left\{\frac{r_1r_2}{\rho^2}\right.\frac{\left(\left|\frac{r_1}{r_2}\right|^n+\left|\frac{r_2}{r_1}\right|^n-2\cos n\overline{\alpha-\beta}\right)\left(\left|\frac{r_1}{r_2}\right|^n+\left|\frac{r_2}{r_1}\right|^n-2\cos n\overline{\alpha+\beta}\right)}{4n^2\sin n\alpha\,.\,\sin n\beta}.\quad(5)'$$

§ 13. A few special cases of this may be recorded. When $r_1 = r_2$, it becomes

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{r}{\rho}\cdot\frac{\cos n\alpha - \cos n\beta}{n\sqrt{(\sin n\alpha \,.\, \sin n\beta}}\right). \quad . \quad . \quad . \quad (6)$$

If at the same time α be made zero and $\beta = \theta$, we ought to get (4); but we must remember that α is not actually to vanish, it is to become very small and equal to $\frac{\rho}{2r}$, which is a sort of compromise between $\frac{\rho}{r}$, the greatest value it could vanish with, and $\frac{0}{r}$, the least. So putting

$$\alpha = \frac{\rho}{2r}, \quad \beta = \theta - \frac{\rho}{2r},$$

(6) becomes

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{r}{n\rho}\cdot\frac{2}{\frac{n\rho}{2r}}\right) = \frac{2}{\pi\kappa\delta}\log\frac{2r}{n\rho},$$

which agrees with (4).

Going back to r_1 and r_2 unequal, let us put both poles on OX—that is, write

$$\alpha = 0 = \frac{\rho}{2r_1} \text{ and } \beta = 0 = \frac{\rho}{2r_2},$$

(5) will become

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{r_1^n - r_2^n}{n^2\rho^2 r_1^{n-1} r_2^{n-1}}\right)^2; \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and this reduces to (2) when r is made infinite.

Similarly if the poles were placed one on OX and the other on OY, we should get

$$\frac{1}{\pi\kappa\delta}\log\frac{(r_1^n + r_2^n)^2}{n^2\rho^2 r_1^{n-1} r_2^{n-1}}; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and this reduces to (3) when $r_1 = r_2 + c = \infty$, and $\theta = \frac{s}{r} = 0$.

One more case is worth mentioning, viz. when one of the poles, say B, is on the angle of the wedge at O. To give this, $r_2 = \rho$ and (β being any thing between 0 and θ, $n\beta$ will be

any thing between 0 and π, say $\frac{\pi}{2}$) $\sin n\beta = 1$, so

$$\Re = \frac{1}{2\pi\kappa\delta} \log \left(\frac{r_1^{2n+1}}{\rho^{2n+1}} \cdot \frac{1}{2n \sin n\alpha} \right). \quad . \quad . \quad (9)$$

If at the same time A is on OX or OY, this becomes

$$\frac{n+1}{\pi\kappa\delta} \log \left\{ \frac{r_1}{\rho} \cdot \left(\frac{\theta}{\pi} \right)^{\frac{1}{n+1}} \right\}. \quad . \quad . \quad . \quad . \quad (10)'$$

A direct application of Cotes's property and equation (B) to this last case gives us as the perfectly accurate expression

$$\frac{n}{\pi\kappa\delta} \log \left\{ \frac{r_1 - \rho_1}{\rho_2} \left(\frac{r_1^n - \rho_2^n}{r_1^n - (r_1 - \rho_1)^n} \right)^{\frac{1}{n}} \right\}, \quad . \quad . \quad (10)$$

whatever be the size of the electrodes, provided that they be taken of such shape as to fit the equipotential lines passing through the two points P and Q to which distances are measured. Both these points are on the line A B, one of them distant ρ_1 from A, the other ρ_2 from B. This expression will reduce to (10)′ when ρ_1 and ρ_2 are regarded as small quantities of the first order.

§ 14. Although all these expressions are proved only when θ is a submultiple of π, yet by continuity they would seem likely to hold true always. If so, we have expressed the resistance of a Riemann's surface of any number of leaves, but all connected at one branch-point O.

General resistance of a "Strip," or regular two-sided polygon, poles anywhere. Fig. 4.

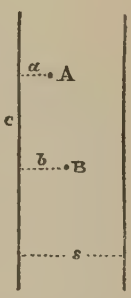
§ 15. The strip being a special case of the wedge, its resistance will follow directly from (5)* by making θ vanish. We must substitute

$$s = r_1\theta, \quad a = r_1\alpha, \quad b = r_2\beta, \quad c = r_1 - r_2,$$

and then make $r_1 = r_2 + c$ infinite, keeping c, a, b, s all finite (fig. 4). The substitutions give us

$$\alpha = \frac{a}{s}\theta, \quad \beta = \frac{b}{s}\frac{r_1}{r_2}\theta, \quad n = \frac{\pi}{\theta} = \frac{\pi r_1}{s};$$

so the resistance (5)′ becomes



* It might be objected that when n is made large, higher powers of ρ in the expansion of $(r-\rho)^n$ may not be neglected, as was done in the process of obtaining (5). This would be true if the size of n were merely due to the shutting up of θ with a constant r: but in our present case r is also large, and the expansion is in descending powers of r.

$$\mathfrak{R} = \frac{1}{2\pi\kappa\delta}\log$$

$$\left\{\frac{s^2}{\pi^2\rho^2}\cdot\frac{\left(\cosh\frac{c}{s}\pi-\cos\frac{a-b}{s}\pi\right)\left(\cosh\frac{c}{s}\pi-\cos\frac{a+b}{s}\pi\right)}{\sin\frac{a\pi}{s}\sin\frac{b\pi}{s}}\right\}. \quad (11)$$

§ 16. For the case when both poles are at the same distance from the sides of the strip, or $a=b$, this becomes

$$\frac{1}{\pi\kappa\delta}\log\left\{\frac{2s}{\pi\rho}\sinh\frac{\pi c}{2s}\left(\frac{\cosh\frac{c\pi}{s}-\cos\frac{2a\pi}{s}}{1-\cos\frac{2a\pi}{s}}\right)^{\frac{1}{2}}\right\}; \quad . \quad (12)$$

and if they are also both in the middle of the strip, it simplifies to

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{s}{\pi\rho}\sinh\frac{\pi c}{s}\right), \quad . \quad . \quad . \quad . \quad . \quad (2)'$$

which is just half (2), as it ought to be. I write out this particularly, because this case has been already studied by Stefan, and experimentally verified by von Obermayr (*Wien. Akad. Ber.* 1869, vol. lx. part 2. p. 245). Stefan, it seems, wrote the expression he obtained thus (merely altering his letters),

$$\frac{1}{\pi\kappa\delta}\log\frac{s}{2\pi\rho}+\frac{1}{\pi\kappa\delta}\log\left(e^{\frac{\pi c}{s}}-e^{-\frac{\pi c}{s}}\right);$$

and this is identical with (2)′.

§ 17. It seems as if expressions like the above might possibly be employed in obtaining the values of certain continued products. Thus to take (12) as an example.

The direct geometrical product for this case, occurring in (β), is the root of

$$\frac{c^2}{\rho^2}\cdot\underline{2a}\,.\,\underline{2s-2a}\,.\,\underline{2s}\,.\,\underline{2s}\,.\,\underline{2s+2a}\,.\,\underline{4s-2a}\,.\,\underline{4s}\,.\,\underline{4s}\,.\,\underline{4s+2a}\,.\,\underline{6s-2a}\ldots.,$$

where $\underline{ks\pm 2a}$ is an abbreviation for $1+\frac{c^2}{(ks\pm 2a)^2}$.

Now one portion of this we know (cf. § 10),

$$\left\{\left(1+\frac{c^2}{2^2s^2}\right)\left(1+\frac{c^2}{4^2s^2}\right)\left(1+\frac{c^2}{6^2s^2}\right)\ldots\right\}^2=\left(\frac{2s}{\pi c}\sinh\frac{\pi c}{2s}\right)^2=\mathrm{A}^2 \text{ say:}$$

and as $A^2\frac{c^2}{\rho^2}$ equals the square of the rational part of the quantity inside the brackets of (12), it follows that the square of the irrational part is equal to the remaining factors of the above product. It may be written

$$\frac{\cosh\frac{2c\pi}{s}-\cos\frac{2a\pi}{s}}{1-\cos\frac{2a\pi}{s}}=1+\frac{\sinh^2\frac{c\pi}{s}}{\sin^2\frac{a\pi}{s}}=\left(1+\frac{c^2}{a^2}\right)\left(1+\frac{c^2}{(s-a)^2}\right)$$
$$\left(1+\frac{c^2}{(s+a)^2}\right)\left(1+\frac{c^2}{(2s-a)^2}\right)\left(1+\frac{c^2}{(2s+a)^2}\right)\ldots,$$

merely putting s instead of $2s$, and a instead of $2a$.

Whether this result is otherwise obvious or not, it will serve as an example of how new products might sometimes be evaluated from resistance-expressions.

General resistance of a circular sector.

§ 18. The resistance of a circular sector containing two poles A and B will be twice the resistance of a wedge with the same angle, but in which, besides the poles A and B, there also exist poles A′ and B′ at the points inverse to A and B with regard to the circle of which the sector is a part; that is, calling R the radius of the sector, $OA'=\frac{R^2}{r_1}$, $OB'=\frac{R^2}{r_2}$. The expression for the resistance will be (5) plus an additional expression

$$\mathfrak{R}=(5)+\frac{1}{2\pi\kappa\delta}\log\frac{\left\{\left|\frac{R^2}{r_1r_2}\right|^n+\left|\frac{r_1r_2}{R^2}\right|^n-2\cos n\overline{\alpha-\beta}\right\}\left\{\left|\frac{R^2}{r_1r_2}\right|^n+\left|\frac{r_1r_2}{R^2}\right|^n-2\cos n\overline{\alpha+\beta}\right\}}{\left(\left|\frac{R}{r_1}\right|^n-\left|\frac{r_1}{R}\right|^n\right)\left(\left|\frac{R}{r_2}\right|^n-\left|\frac{r_2}{R}\right|^n\right)\left(\left|\frac{R}{r_1}\right|^{2n}+\left|\frac{r_1}{R}\right|^{2n}-2\cos 2n\alpha\right)^{\frac{1}{2}}\left(\left|\frac{R}{r_2}\right|^{2n}+\left|\frac{r_2}{R}\right|^{2n}-2\cos 2n\beta\right)^{\frac{1}{2}}}$$

§ 19. When the angle of the sector vanishes by R becoming infinite, we get the case of a strip bounded towards one end, or what may be called an isosceles triangle whose equal angles are $\frac{\pi}{2}$. The pole A being at a distance c_1 from the base and a from one of the sides, while B is at a distance b from the

same side, c_2 from the base, the above expression reduces to

$$R=(11)+\frac{1}{2\pi\kappa\delta}\log$$

$$\frac{\left(\cosh\frac{c_1+c_2}{s}\pi-\cos\frac{a-b}{s}\pi\right)\left(\cosh\frac{c_1+c_2}{s}\pi-\cos\frac{a+b}{s}\pi\right)}{2\sinh\frac{\pi c_1}{s}\sinh\frac{\pi c_2}{s}\sqrt{\left(\cosh\frac{2\pi c_1}{s}-\cos\frac{2a\pi}{s}\right)}\sqrt{\left(\cosh\frac{2\pi c_2}{s}-\cos\frac{2b\pi}{s}\right)}}, \quad (14)$$

where the c in (11) may be written c_1-c_2 for symmetry.

It may be noticed that the additional quantity in (14) vanishes when c_1 and c_2 are infinite; but becomes the same as (11) when c_1 and c_2 are made small and equal to $\frac{\rho}{2}$; and this is just what it ought to do.

§ 20. The quantity which is added to (11) to give (14) may be called the "effect of the boundary" which limits the strip at one end. If we added a boundary to the other end of the strip also, it would become a rectangle of breadth s and length c_1+c_3 or c_2+c_4; and by adding another quantity to (11) similar to the above, but with c_3 and c_4 instead of c_1 and c_2 (that is, by adding a quantity which approximates to the effect of the new boundary), we should obtain an approximation to the resistance of a rectangle, which is a pretty close one if the c are larger than the s. Such an approximate expression, however, has no particular interest. It is easy to write down the products occurring in (α) for the general case of a rectangle; but their evaluation does not appear to be so simple.

Distribution of potential in a "wedge" containing any number of point poles.

§ 21. All the flow-conditions in a wedge whose angle is $\frac{\pi}{n}$ are determined completely by writing out the particular form assumed by the general expression (A)′, § 8, for this case. The polar coordinates of the sources being (r_1, α), $(r'_1, \alpha')\ldots$, and of the sinks being (r_2, β), $(r'_2, \beta')\ldots$, the potential at any point (r, ϕ) is

$$V=\frac{q}{4\pi\kappa\delta}\log$$

$$\frac{(r^{2n}-2r^n r_2^n\cos n\overline{\phi-\beta}+r_2^{2n})(r^{2n}-2r^n r_2^n\cos n\overline{\phi+\beta}+r_2^{2n})}{(r^{2n}-2r^n r_1^n\cos n\overline{\phi-\alpha}+r_1^{2n})(r^{2n}-2r^n r_1^n\cos n\overline{\phi+\alpha}+r_1^{2n})} \quad (15)$$

+ similar terms with accented coordinates for every other pair of poles which the sheet may contain.

When the wedge becomes a "strip" of breadth s, the above expression gives, as the potential of any point (x, y),

$$V = \frac{q}{4\pi\kappa\delta}\log \frac{\left(\cosh\frac{y-y_2}{s}\pi - \cos\frac{x-x_2}{s}\pi\right)\left(\cosh\frac{y-y_2}{s}\pi - \cos\frac{x+x_2}{s}\pi\right)}{\left(\cosh\frac{y-y_1}{s}\pi - \cos\frac{x-x_1}{s}\pi\right)\left(\cosh\frac{y-y_1}{s}\pi - \cos\frac{x+x_1}{s}\pi\right)} \quad (16)$$

+ &c.,

where the sources are (x_1, y_1), $(x'_1, y'_1)\ldots$, the sinks (x_2, y_2), $(x'_2, y'_2)\ldots$, and where one side side of the strip is taken as the axis of y.

General form of the resistance-expression for two poles.

§ 22. It is convenient at this point to notice the general form of the resistance-expression for two poles A and B in any bounded plate. It may always be written in the form

$$\frac{c}{\pi\kappa\delta}\log\left(\frac{AB}{\rho}\cdot Q\right), \quad \ldots\ldots \quad (\gamma)$$

where Q is a numerical quantity which depends on the general form of the boundaries of the plate, and on the position of the poles with respect to those boundaries; while c is a number which depends only on that part of the boundary which is infinitely near a pole. As long as the poles are not placed on the edge of the plate, $c=1$ and is unaffected by any change in the boundary; but if either pole is placed on the edge, the angle on which it is placed determines c,—the general law being that if A is on an angle $\frac{\pi}{m}$, and B on an angle $\frac{\pi}{n}$, then $c=m+n$. (When both poles are inside the plate, both angles equal 2π, and therefore $c=1$, as stated above.)

It is unnecessary to prove this rule formally; but it is a consequence of the necessary condition that A and B must be of equal strength in the limited sheet; for this condition requires that if they are on angles $\frac{2\pi}{2m}$ and $\frac{2\pi}{2n}$ respectively, their

strengths in the unlimited sheet must be in the ratio of $2m : 2n$, and accordingly the quantity $\frac{AB}{\rho}$ in (α) § 8 will occur to the $2(m+n)$th power.

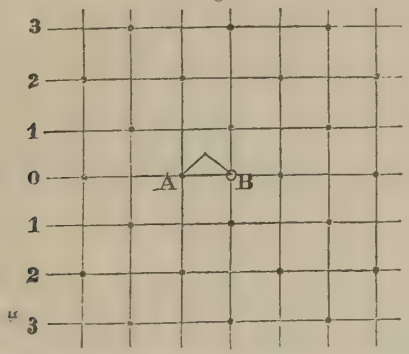
Hence, in the process of finding the resistance of any plane conductor containing two small electrodes, the determination of Q is the only difficulty. We have found it for the general polygon of two sides; let us proceed to find it for a few triangles.

Resistance of an isosceles right-angled triangle. Poles on the equal angles.

§ 23. This case was in reality the first figure with rectilinear boundaries which I attempted. The positions of the images of A are shown in fig. 5; they are on the corners of squares covering all the plane. The images of B will be similarly arranged, every source being surrounded by four sinks.

To determine the value of the product $\left(\frac{AB}{\rho} . Q\right)$ in the resistance-expression (β) (§ 8), take the images in rows, and find the product for each row separately (cf. § 9). Call the line A B,

Fig. 5.



Images of the pole A in an isosceles right-angled triangle.

fig. 5, row 0; the two rows one on either side of A B call rows 1; row 2 will be the row next beyond each of these; and so on, the images being evidently symmetrical with respect to the line A B. The whole product Q will then equal $Q_0, Q_1^2, Q_2^2 \dots$, where Q_r stands for the product of the $\frac{A_r B}{A_r A}$'s in one row r.

From the figure we see that

$$Q_0=\frac{1.3.3.5.5.7\ldots}{2.2.4.4.6.6\ldots} \qquad =\frac{2}{\pi}=\frac{1}{\varpi(0)},$$

$$Q_1^2=\frac{1^2}{1^2+1^2}\cdot\frac{2^2+1^2}{1^2+1^2}\cdot\frac{2^2+1^2}{3^2+1^2}\cdot\frac{4^2+1^2}{3^2+1^2}\cdot\frac{4^2+1^2}{5^2+1^2}\cdots =1^2.\varpi^2(1),$$

$$Q_2^2=\frac{1^2+2^2}{2^2}\cdot\frac{1^2+2^2}{2^2+2^2}\cdot\frac{3^2+2^2}{2^2+2^2}\cdot\frac{3^2+2^2}{4^2+2^2}\cdots \qquad =\frac{1}{2^2\varpi^2(2)},$$

$$Q_3^2=\frac{3^2}{1^2+3^2}\cdot\frac{2^2+3^2}{1^2+3^2}\cdot\frac{2^2+3^2}{3^2+3^2}\cdots \qquad =3^2\varpi^2(3),$$

. . . . . .

and in general

$$Q_x^{\pm 1}=x\varpi(x),$$

where the index is to be taken positive when x is odd, negative when x is even; and where $\varpi(x)$ stands for the product

$$\frac{2^2+x^2}{1^2+x^2}\cdot\frac{4^2+x^2}{3^2+x^2}\cdot\frac{6^2+x^2}{5^2+x^2}\cdots\frac{1}{\sqrt{(\infty^2+x^2)}},$$

of which Wallis's expression is the particular case when $x=0$.

The entire product Q also shows an evident resemblance to Wallis's form, being

$$Q=\frac{2}{\pi}\left(\frac{1\varpi(1).3\varpi(3)\ldots}{2\varpi(2).4\varpi(4)\ldots}\right)^2.$$

Further than this I was unable to proceed; so I showed the products to Mr. J. W. L. Glaisher during the Bristol Meeting of the British Association; and he very kindly told me how to evaluate the product denoted above by $\varpi(x)$, and subsequently worked out the compound product Q. Taking the well-known trigonometrical identities

$$\sin\frac{\pi x}{2}=\frac{\pi x}{2}\left(1-\frac{x^2}{2^2}\right)\left(1-\frac{x^2}{4^2}\right)\left(1-\frac{x^2}{6^2}\right)\cdots,$$

$$\cos\frac{\pi x}{2}=\left(1-\frac{x^2}{1^2}\right)\left(1-\frac{x^2}{3^2}\right)\left(1-\frac{x^2}{5^2}\right)\cdots,$$

Mr. Glaisher divided one by the other after putting $x\sqrt{-1}$ for x; he thus obtained

$$\tan\frac{i\pi x}{2}=\frac{i\pi x}{2}\cdot\frac{2^2+x^2}{1^2+x^2}\cdot\frac{4^2+x^2}{3^2+x^2}\cdots\frac{1^2.3^2.5^2\ldots}{2^2.4^2.6^2\ldots}$$

$$=\frac{i\pi x}{2}.\varpi(x).\frac{2}{\pi},$$

whence

$$x\varpi(x) = \frac{1}{i}\tan\frac{i\pi x}{2} = \tanh\frac{\pi x}{2}\text{*}.$$

This result gives us

$$Q = \frac{2}{\pi}\left(\frac{\tanh\frac{\pi}{2}\cdot\tanh\frac{3\pi}{2}\cdots}{\tanh\frac{2\pi}{2}\cdot\tanh\frac{4\pi}{2}\cdots}\right)^2.$$

The part inside the brackets may be written

$$\sqrt{\frac{\pi Q}{2}} = \frac{1-e^{-\pi}}{1+e^{-\pi}}\cdot\frac{1-e^{-3\pi}}{1+e^{-3\pi}}\cdots\frac{1+e^{-2\pi}}{1-e^{-2\pi}}\cdot\frac{1+e^{-4\pi}}{1-e^{-4\pi}}\cdots;$$

and this Mr. Glaisher saw at once was a special case of Jacobi's products; two of which (being those required in this paper) I write down here—

$$\frac{1-q}{1+q}\cdot\frac{1-q^3}{1+q^3}\cdot\frac{1-q^5}{1+q^5}\cdots = k'^{\frac{1}{4}}, \quad \ldots\ldots \quad (\delta)$$

$$\frac{1-q^2}{1+q^2}\cdot\frac{1-q^4}{1+q^4}\cdot\frac{1-q^6}{1+q^6}\cdots = \left(\frac{2\sqrt{k'}K}{\pi}\right)^{\frac{1}{2}}; \quad \ldots \quad (\epsilon)$$

q stands for $e^{-\pi\frac{K'}{K}}$, K having its ordinary meaning of

$$\int_0^{\frac{\pi}{2}} \frac{d\theta}{\sqrt{(1-k^2\sin^2\theta)}}.$$

Taking the modulus-angle 45° so that $k=k'=\frac{1}{\sqrt{2}}$ and $K=K'=K_0$ say, and then dividing (δ) by (ϵ), there results the product required,

$$\sqrt{\frac{\pi Q}{2}} = \sqrt{\frac{\pi}{2K_0}}.$$

Hence $Q=\frac{1}{K_0}$, and the resistance of a triangle with each electrode on an angle of 45° is

$$R = \frac{8}{\pi\kappa\delta}\log\left(\frac{AB}{\rho}\cdot\frac{1}{K_0}\right). \quad \ldots\ldots \quad (17)$$

* Mr. Glaisher also obtained an expression for the more general product $\frac{2^n+x^n}{1^n+x^n}\cdot\frac{4^n+x^n}{3^n+x^n}\cdots$, which he has communicated to the Mathematical Society.

The numerical value of K_0 from Legendre's Tables is

1·854 074 677 301.

§ 24. If one writes out (17) in two parts,

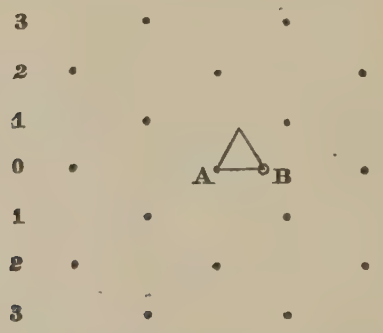
$$\frac{8}{\pi\kappa\delta}\log\frac{AB}{\rho}-\frac{8}{\pi\kappa\delta}\log\int_0^{\frac{\pi}{2}}\frac{d\theta}{\sqrt{(1-\frac{1}{2}\sin^2\theta)}}, \quad . \quad (17)'$$

the first term is the resistance of a segment of a circle with base AB and with its arc touching the two sides of the triangle at A and B; and the second term may be called the effect of the "coquadrant"* by which the triangle exceeds the segment in area. But one must not imagine that this term expresses the resistance of this figure. The fact is that its resistance cannot be found by any consideration of (17)′, for reasons which shall be stated, § 30, footnote. It is worth while to notice the arrangement of poles and flow-lines which would produce this coquadrant figure in an unlimited sheet; but they will come better later.

Resistance of an equilateral triangle. Poles on two of the angles.

§ 25. The images of A for this case are shown in fig. 6,

Fig. 6.



Images of the pole A in an equilateral triangle.

being on the vertices of equilateral triangles $\sqrt{3}$ times the

* I call it a *coquadrant* because it is the excess of a square over the quadrant whose radius is a side of the square: more generally the figure enclosed by any circular arc and two tangents might be called a *cosector*; it would be the excess of an isosceles cirquadrilateral over the inscribed sector, and it only differs from a sector in having the equal angles 0° instead of 90°.

linear dimensions of the original one. Take the images in rows as before (§ 23), calling the line A B row 0, and find the product Q_s for each row separately.

$$Q_0 = \frac{2.4.5.7.8.10\ldots}{3.3.6.6.9.9\ldots} = \frac{3\sqrt{3}}{2\pi} = \sqrt{0^2\phi(0)\psi(0)},$$

$$Q_1^2 = \frac{1^2+3}{3^2+3}\cdot\frac{5^2+3}{3^2+3}\cdot\frac{7^2+3}{9^2+3}\cdot\frac{11^2+3}{9^2+3}\cdot\frac{13^2+3}{15^2+3}\cdots = \phi(\sqrt{3}),$$

$$Q_2^2 = \frac{2^2+2^2.3}{2^2.3}\cdot\frac{4^2+2^2.3}{6^2+2^2.3}\cdot\frac{8^2+2^2.3}{6^2+2^2.3}\cdot\frac{10^2+2^2.3}{12^2+2^2.3}\cdots = \psi(2\sqrt{3}),$$

$$Q_3^2 = \frac{1^2+3^2.3}{3^2+3^2.3}\cdot\frac{5^2+3^2.3}{3^2+3^2.3}\cdot\frac{7^2+3^2.3}{9^2+3^2.3}\cdots = \phi(3\sqrt{3}),$$

. . . . . ;

and

$$Q = \frac{3\sqrt{3}}{2\pi}\,\phi(\sqrt{3})\psi(2\sqrt{3})\phi(3\sqrt{3})\psi(4\sqrt{3})\ldots.$$

Now

$$\phi(x) = \frac{1^2+x^2}{3^2+x^2}\cdot\frac{5^2+x^2}{3^2+x^2}\cdot\frac{7^2+x^2}{9^2+x^2}\cdots = \frac{1}{4}\cdot\frac{\cosh\frac{\pi x}{2}}{\cosh^3\frac{\pi x}{6}}$$

$$= \frac{1+3\tanh^2\frac{\pi x}{6}}{4},$$

this result being evident if numerator and denominator are multiplied by

$$3^2+x^2.\,9^2+x^2.\,15^2+x^2\ldots;$$

and similarly

$$\psi(x) = \frac{2^2+x^2}{x^2}\cdot\frac{4^2+x^2}{6^2+x^2}\cdot\frac{8^2+x^2}{6^2+x^2}\cdots = \frac{1}{4}\cdot\frac{\sinh\frac{\pi x}{2}}{\sinh^3\frac{\pi x}{6}}$$

$$= \frac{1+3\coth^2\frac{\pi x}{6}}{4}.$$

Hence

$$Q = \frac{3\sqrt{3}}{2\pi}\cdot\frac{1+3\tanh^2\frac{\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\tanh^2\frac{3\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\tanh^2\frac{5\pi}{2\sqrt{3}}}{4}\cdots$$

$$\times\frac{1+3\coth^2\frac{2\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\coth^2\frac{4\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\coth^2\frac{6\pi}{2\sqrt{3}}}{4}\cdots$$

This product I sent to Mr. Glaisher; and he returned it reduced to a product of two theta-functions. He proved the two following identities :—

$$P_1=\frac{1+m\tanh^2\theta}{1+m}\cdot\frac{1+m\tanh^2 3\theta}{1+m}\cdot\frac{1+m\tanh^2 5\theta}{1+m}\cdots$$
$$=\sqrt{\frac{\pi}{2K}}\,\Theta\left(\frac{2Kx}{\pi}\right)$$

and

$$P_2=\frac{1+m\coth^2 2\theta}{1+m}\cdot\frac{1+m\coth^2 4\theta}{1+m}\cdot\frac{1+m\coth^2 6\theta}{1+m}\cdots$$
$$=\frac{1}{\cos x}\sqrt{\frac{\pi^3}{(2K)^3kk'}}\cdot H\left(\frac{2Kx}{\pi}+K\right),$$

where

$$\cos 2x=\frac{m-1}{m+1}\text{ and }2\theta=\pi\frac{K'}{K}.$$

In our present case

$$m=3\text{ and }\theta=\frac{\pi}{2\sqrt{3}};$$

so

$$K=\sqrt{3}K',\ k=\sin 75^\circ,\text{ and }x=\frac{\pi}{6}.$$

Hence

$$P_1=\sqrt{\frac{\pi}{2K}}\,\Theta(\tfrac{1}{3}K),\quad\frac{\sqrt{3}}{2}P_2=\sqrt{\frac{\pi^3}{8K^3kk'}}\,H(\tfrac{2}{3}K),$$

and

$$Q=\frac{3\sqrt{3}}{2\pi}P_1P_2=\frac{3\pi}{4K^2\sqrt{k'}}\Theta(30^\circ)\Theta_1(60^\circ)\text{ (mod. angle }75^\circ),$$

writing $\Theta_1(x)$ for $\frac{1}{\sqrt{k}}H(x)$.

From the British-Association Tables

$$\log\frac{1}{K^2\sqrt{k'}}=\bar{1}\cdot4091498986,$$
$$\log\Theta(30^\circ)=\bar{1}\cdot9223413942,$$
$$\log\Theta_1(60^\circ)=\ \cdot0491498189;$$

so

$$\log_{10}Q\ =\bar{1}\cdot7528522478,$$

or

$$Q=\frac{1}{1\cdot76664}\text{ about,}$$

and the resistance of the triangle is

$$R = \frac{6}{\pi\kappa\delta} \log\left(\frac{AB}{\rho} \cdot Q\right) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Manner in which the image-method fails for an angle of 120°.

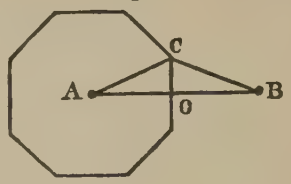
§ 26. We found in § 5 that the only isosceles triangles which could be treated by the method of images were those with the equal angles either 0°, 45°, 60°, 90°, or 180°; and of these all except the first have been already done in the course of this paper (§§ 23, 25, 19, 10), and the first shall be considered in the next section. But suppose we attempted the triangle with equal angles 30°, which is apparently a very simple case; the images of the source A (on one of the equal angles) would be readily placed on the corners of regular hexagons; but they would be symmetrically situated with respect to the middle line of the triangle, and hence when the images of the sink B came to be placed they would coincide with those of A and would blot them all out of the sheet. Or if we overlook this and apply the expression (β) to the images of A, then, because of their symmetry with respect to the triangle, the product Q (§§ 8 & 22) will equal 1; which can be proved to be wrong (§ 27). This failure, caused by the presence of the angle 120°, is one that cannot, even apparently, be got over by silvering both sides of the boundaries (§ 4); for, in order to arrange poles in an unlimited sheet so as to be symmetrical with respect to all three sides of the triangle, it is necessary that one and the same point shall be at the same time both a source and a sink. Dr. Henrici suggests that this is possible if the plane consists of two leaves, and recommends in general, whenever both sides of a boundary have to be silvered and some of the images are *real* (that is, occur in the given plate itself), that these real images be put in another leaf of the plane. It seems just possible that some such contrivance might enable the image-method to be applied to polygons whose angles are not integral submultiples of π.

Empirical formula for the resistance of a general isosceles triangle. Poles on the equal angles.

§ 27. Consider a regular polygon of n sides, with one electrode

(radius ρ), A, fig. 7, at its centre, and with its entire periphery maintained at one potential. The resistance R_n of such a polygon to radial flow is evidently something between that of its inscribed and that of its circumscribing circle; in other words,

Fig. 7.



$$\frac{1}{2\pi\kappa\delta}\log\frac{AO}{\rho} < R_n < \frac{1}{2\pi\kappa\delta}\log\frac{AC}{\rho}.$$

Now the resistance R of the isosceles triangle A B C (fig. 7) equals twice the resistance of the triangle A O C, which again equals $2n$ times the resistance of the polygon. Hence, writing

$$AC = AO\sec CAO = \tfrac{1}{2}AB\sec\frac{\pi}{n},$$

$$\frac{2n}{\pi\kappa\delta}\log\frac{AB}{2\rho} < R < \frac{2n}{\pi\kappa\delta}\log\left(\frac{AB}{2\rho}\sec\frac{\pi}{n}\right);$$

or, calling the angle CAO θ, we may write the resistance of any isosceles triangle with equal angles θ,

$$R = \frac{2}{\theta\kappa\delta}\log\left(\frac{AB}{\rho}\frac{1}{f(\theta)}\right), \quad . \quad . \quad . \quad . \quad (19)$$

where $f(\theta)$ is something between $2\cos\theta$ and 2. Hence the limit of Q when the angles of the triangle vanish is $\frac{1}{2}$. Moreover when the angles are 30°, $f(\theta)$ must lie between 2 and $\sqrt{3}$; it cannot, therefore, be 1 as the product of images (§ 26) would lead us to believe.

Looking at the few values of $f(\theta)$ which are known, one may notice how nearly they divide the interval allowed to them, $2-2\cos\theta$, in the ratio 1 : 3. The quantity which actually does this is $\frac{3+\cos\theta}{2}$; and this quantity agrees with the known values of $f(\theta)$ to an extent shown in the Table.

θ.	$f(\theta)$.	$\frac{3+\cos\theta}{2}$.
0°	2·0	2·0
45	1·854	1·853
60	1·766	1·75
90	1·57	1·50
180	1·0	1·0

The maximum divergence appears to occur about when $\theta = 90°$.

The empirical formula, then,

$$\frac{2}{\theta\kappa\delta}\log\left(\frac{AB}{\rho}\cdot\frac{2}{3+\cos\theta}\right) \quad . \quad . \quad . \quad . \quad . \quad (19)'$$

gives the resistance of any isosceles triangle with poles on the equal angles θ with sufficient accuracy for a practical purpose; and it becomes very accurate indeed when the equal angles are small. The value of Q indicated by it for the case $\theta = 30°$ is $\frac{1}{1{\cdot}9330}$; and I venture to think that the real value will be found to differ from this only in the last place of decimals.

The resistance to the flow of electricity from a central electrode of radius ρ to the periphery of a regular polygon of n sides is, to the same degree of approximation as the above,

$$\frac{1}{2\pi\kappa\delta}\log\left(\frac{r}{\rho}\cdot\frac{4}{3+\cos\frac{\pi}{n}}\right), \quad . \quad . \quad . \quad . \quad . \quad (20)$$

r being the radius of the inscribed circle.

§ 28. And here I would remark that the thickness (δ) of the plate in which the flow takes place has never been limited in any way; so the plate may extend itself into a cylinder of any length, provided the point poles extend themselves into lines at the same time. Also, though we are using the language of dynamic electricity only, yet the resistance obtained applies equally well to heat if we substitute hot and cold bodies for sources and sinks, temperature for potential, and isothermals for equipotential lines. Further, by reason of the analogy between conductivity and inductive capacity, we obtain at the same time the inductive capacity of a dielectric medium exposed to conductors at different potentials which correspond to the poles in the dynamic problem.

Resistance of some squares and right-angled triangles.

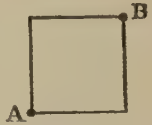
§ 29. The forms assumed by the resistance-expressions (§ 8) for the case of a square plate with the poles in certain definite positions may be recorded, together with the products which lead to them. The resistance seems always to be of the

form

$$R=\frac{m+n}{\pi\kappa\delta}\log\left(\frac{AB}{\rho}\cdot\frac{2^{\alpha}}{K_0}\right), \quad . \quad . \quad . \quad . \quad (21)$$

where the poles A and B are on angles $\frac{\pi}{m}$ and $\frac{\pi}{n}$ respectively, and where α takes different values in different cases, and is the only thing which varies. K_0 still stands for the first complete elliptic integral with modulus $\frac{1}{\sqrt{2}}$.

Fig. 8.



For the case represented in fig. 8 the value of α is zero, because the resistance of such a square is just half that of the right-angled triangle (17) § 23.

Fig. 9.

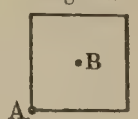
When the poles are as in fig. 9, $\alpha=\frac{1}{4}$; the product in (β) which leads to the result consists of terms $\coth^2\frac{\pi x}{2}$, where x takes the values 2, 4, 6, ...

Fig. 10.

The case of fig. 10 gives us $\alpha=\frac{1}{2}$, the product being $\Pi\left(\coth^2\frac{\pi x}{2}\right)$, with x successively 1, 2, 3, 4, &c.

The case of fig. 11, being unsymmetrical in sources and sinks, requires the complete expression (α) § 8; and, because the pole at the corner of the square has to be four times as strong as the other in the infinite sheet, the two factors inside the brackets of (α) occur to different powers; in other words, calling the factors P_1 and P_2, we shall have

Fig. 11.



$$Q^5=P_1P_2^4.$$

Now P_1, the product referring to the images of the pole at the centre, is the old one whose value is $\frac{1}{K_0}$ (§ 23). But the product for the images of the corner pole will be found to be

$$P_2=\frac{2\sqrt{2}}{\pi}\Pi\left(\coth\frac{\pi x}{2}\coth\frac{\pi x}{4}\right)\Pi\left(\frac{\coth\frac{\pi x'}{2}}{\coth\frac{\pi x'}{4}}\right),$$

where x is to take the successive values 4, 8, 12, ..., and x' the values 2, 6, 10, ...

Writing this product P_2 in the form

$$\frac{2\sqrt{2}}{\pi} \cdot \frac{\tanh\frac{\pi}{2} \cdot \tanh\frac{3\pi}{2} \cdots}{\tanh\frac{2\pi}{2} \cdot \tanh\frac{4\pi}{2} \cdots} \cdot \coth\pi \cdot \coth 2\pi \cdot \coth 3\pi \cdots,$$

it is brought into connexion with (δ) and (ϵ) (§ 23); and its value is thus found to be

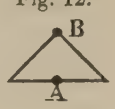
$$P_2 = \frac{2\sqrt{2}}{\pi}\sqrt{\frac{\pi}{2K_0}}\sqrt{\frac{\pi}{2^{\frac{1}{2}}K_0}} = \frac{2^{\frac{5}{8}}}{K_0}.$$

Hence $$Q^5 = \frac{2^{\frac{5}{2}}}{K_0^5}, \text{ or } Q = \frac{\sqrt{2}}{K_0}.$$

In other words, the resistance of a square plate with the poles arranged as in fig. 11 is given by (21), if for $m+n$ we read its value $\frac{5}{2}$, and consider α equal to $\frac{1}{2}$.

One more distinct case may be mentioned, namely the right-angled triangle shown in fig. 12. This also requires two factors raised to different powers; and the result is the expression (21) with $\alpha = \frac{1}{6}$.

Fig. 12.



[To be continued.]

V. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

[Continued from p. 14.]

IV.

Separation of Ice, or of a Hydrate, or of the Anhydrous Salt, from solutions of Salts below 0° C.

§ 123. Very many determinations have been made of the solubility of various salts in water at temperatures ranging from 0° C. to the temperature of ebullition of the saturated salt solution. To Gay-Lussac, to Kremers, to Regnault, and others are due several series of exact determinations in this direction of research. But the examination of the phenomena of solidification which take place in salts of certain strengths at temperatures below 0° C. has suffered comparative, almost complete, neglect. And this appears to

have arisen partly from the circumstance that it has been asserted by some philosophers, and denied by others entitled to equal respect, that when a solution of a salt below 0° C. begins to solidify by loss of heat, the solid formed is pure ice. It has been my privilege to reconcile the opposing views by the discovery of the fact which I trust now to have fully established, that when a salt solution which is already any fraction of a degree below 0° C. is cooled, one of three things must happen; and which of them happens is determined with the same salt by the strength of the solution.

1. In all solutions weaker than the cryohydrate, ice is formed, at temperatures which are lower according as the solution is richer in salt.

2. In solutions of a certain strength (namely that of the cryohydrate), combination of the salt and water take place in definite ratio and at a constant temperature. The solution is therefore a melted cryohydrate, and solidifies as a whole.

3. When solutions stronger than the cryohydrate, below 0° C., are cooled, either the anhydrous salt or some hydrate richer in salt than the cryohydrate separates.

It follows that the cryohydrate may, and indeed must inevitably be reached both by cooling a solution weaker than the cryohydrate (ice separates, the solution strengthens, the temperature sinks), and by cooling a solution stronger than the cryohydrate (anhydrous salt or a hydrate richer than the cryohydrate separates, the solution weakens, the temperature sinks). Assuming as a fact that which will be abundantly proved, namely that every salt which is soluble above 0° C. is also soluble below 0° C. (we shall see that there is even no quantitative discontinuity at 0° C. in the solubility), it follows immediately that a solution of any degree of strength whatever gives rise on cooling, sooner or later, to a liquid which remains unsolidified until the proper ratio and temperature is reached, and then solidifies in that constant ratio and at that constant temperature. From a solution of the strength of the cryohydrate nothing separates until the proper temperature is reached. And then, however rapid the absorption of heat may be, the temperature never sinks lower until solidification is complete.

§ 124. I propose in the present communication (1) to trace the history of solutions weaker than the cryohydrates as they

yield ice on cooling, and (2) to examine the separation of anhydrous salts or hydrates richer than the cryohydrates when solutions richer than the cryohydrate are cooled. With regard to the first of these branches of inquiry, the only experiments in this direction which I have described are those relating to chloride of sodium in § 10, and those concerning spirits o wine in § 96.

A solution of a salt below 0° C. which is stronger than the cryohydrate, may be viewed as a solution in the cryohydrate, either of a hydrate richer than the cryohydrate or of the anhydrous salt. A solution of a salt below 0° C. which is weaker than the cryohydrate may be properly regarded as a solution of ice in the cryohydrate. A solution of chloride of sodium stronger than its cryohydrate may be also regarded as a solution of the subcryohydrate, Na Cl 2 H_2 O (?), in the cryohydrate (§ 15).

Just as a given weight of water dissolves at temperatures above 0° C., with rare exceptions, more of a salt the higher the temperature, so a given weight of the cryohydrate dissolves more ice at higher temperatures, below 0° C., than at lower ones. The weaker a given weight of a salt solution below 0° C. is, the smaller is the weight of the cryohydrate in it, and accordingly the less is the weight of ice which the given weight of solution is capable of dissolving. Experimentally, this appears in the results of all my experiments to be described below, that the stronger a solution of any given salt is (being weaker than the cryohydrate), the lower is the temperature below 0° C. to which it must be brought in order to yield ice ; and the stronger a solution of any given salt is (being stronger than the cryohydrate), the less need its temperature be depressed in order to yield the anhydrous salt, or a hydrate richer in salt than the cryohydrate. And, as before stated, the latter kind of separation is quite continuous with the separation of such bodies at temperatures above 0°, such as is exhibited in the ordinary Tables of solubilities referred to in § 123.

§ 125. Almost all the numerical results are represented graphically in fig. 1. The abscissæ are in all cases the percentages of the anhydrous salt in the water. The ordinates, − or +, are the temperatures Centigrade below or above 0° C. at which solid matter begins to separate on cooling the solu-

tion. The point of reflexure (that is, the lowest point of each tracing) shows the temperature at which the particular cryohydrate is formed, and also the percentage of anhydrous salt in the cryohydrate. The left-hand branches of the tracings exhibit the temperature at which ice separates from solutions of the respective salts of the corresponding percentage composition. The right-hand branch of each tracing shows the temperatures at which the anhydrous salt or a hydrate richer than the cryohydrate is separated. The parts of these branches above the zero-line show the ordinary solubility of the same salts above 0°. The figure is reduced from my drawing, in which the percentages and tenths were centimetres and millimetres; and the degrees C. and their tenths were also centimetres and millimetres. The actual observations, being dotted off, were joined by straight lines.

§ 126. *General remarks on the experiments.*—Whenever possible, the solutions of the salts examined were made by dissolving weighed quantities of the anhydrous pure salt in quantities of water measured from a Mohr's burette. The grammes and centimetres were those of the percentages; that is, to form a 20-per-cent. solution, 20 grms. of the salt and 80 cubic centims. of distilled water were employed. Now and then a control mixture formed by weighing only was examined; but it appeared that the sources of error introduced by measuring instead of weighing the water were vanishingly small compared with the unavoidable errors of observation, notably those mentioned in the next paragraph.

Supersaturation.—With every salt solution from which we wish to get solidification by means of cooling, we have to guard against supersaturation. The notion that in order to start the crystallization of a supersaturated solution crystals must be present in the air identical in chemical kind with those ready to be formed in the solution, seems to be disproved by the fact that supersaturation in regard to ice is of the very commonest occurrence. In many cases a salt solution which should yield ice at a temperature $-t°$ refuses to do so until $-(t° + 5°$ or $6°)$ is reached; then ice-crystals are formed through the mass and the temperature rises. Although we may indeed imagine ice-crystals to be floating in the air about the surface of the cryogen, we can scarcely conceive these microscopic crystals to

Fig. 1.

10
20
30
40
50
60
KBr
M_2SO_4
$AgNO_3$
KBr
NH_4Cl
$(NH_4)SO_4$
NH_4NO_3
NaCl
KI
HCl
C_2H_6O
$CaCl_2$

travel unmelted through the surrounding air, which may be at 10° or 15° C., so as to reach the liquid. And if it be argued that the origin of the ice-crystals may be at or near the surface of the salt solution in the experimental tube, I reply that crystallization from a supersaturated solution occurs both when it is covered with a layer of oil and when only the lower part of such a solution is acted on by the cryogen.

Method of observation.—Since the separation of ice strengthens the solution, it is necessary to determine the temperature of the very beginning of the ice-formation. The salt solution is cooled in a test-tube until some ice is formed; this is very nearly completely remelted under constant stirring with the thermometer, and then the tube is plunged momentarily into the cryogen. The minute spicula of ice so formed are again nearly remelted. The mean of four or five readings of the thermometer when the minute quantity of ice begins to increase is taken as the true temperature of ice-formation. In order to save time and start the crystallization of ice in a solution which one has reason to suppose is supersaturated with ice, the thermometer-bulb may be plunged into the cryogen and rapidly wiped dry, or into the mercury-cup to be described immediately. It soon becomes clothed with a film of ice-crystals from the moisture of the air. These are indeed almost invisible, and far too small in quantity to alter the strength of the salt solution when brought into contact with it, but amply sufficient to determine the separation of ice if the solution be supersaturated in regard to that body.

When the tube containing the salt solution is plunged into the cryogen till crystallization begins and then removed, portions of the cryogen adhering to the tube may carry the ice-formation too far, and by soiling obscure the tube. It is therefore found convenient to have standing in the freezing-mixture a short wide-mouthed bottle of mercury, and for the final observations to plunge the tube into this and so avoid soiling.

The solutions stronger than the cryohydrate were treated in a similar manner.

For the solubilities of the various salts at 0° I kept the solutions, previously saturated at 12° C., for three hours at 0°, and determined the strengths by evaporation &c., in some cases by determination of one constituent by the usual chemical means. I find these latter determinations agree very closely with those

of Kremers throughout. Indeed, as will be seen, we seldom differ more than 0·3 per cent. For the determination of the temperatures above 0° C. at which salts and their hydrates separate, I have found, contrary to my anticipations, the more exact method to be in most cases to warm a given weight of the salt with its proper percentage of water in a stoppered bottle till solution was effected, and then by repeated observation find the temperature of incipient crystallization, rather than attempt to keep the water and salt for a length of time at a constant temperature and then determine the strength. The latter method, however, is of course especially available for 0° and 100° C.

§ 127. *Separation of Ice, of Subcryohydrate and of* NaCl *from solutions of that salt.*—The following Table (XVI.) shows the temperature below 0° C. at which ice begins to be separated from solutions of common salt of different strengths. In selecting these strengths I have chosen several close to the critical points, namely to that of distilled water, to that of the cryohydrate, and to that of saturation. And in the case of other salts I have, as far as possible, examined solutions of the same percentage-weight strengths. The ascent (see fig. 1. NaCl) is so steep from the cryohydrate to 0° C. that I have only been able to introduce one observation. As my determination for 0° C. was 26·27 (§ 11), and Poggiale's was 26·28, I have no hesitation in adopting Poggiale's for +25° and +40°.

TABLE XVI.

NaCl per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which a solid is formed.	Nature of solid.
1	99	− 0·3	Ice.
2	98	− 0·9	,,
3	97	− 1·5	,,
4	96	− 2·2	,,
7	93	− 4·2	,,
10	90	− 6·6	,,
13	87	− 9·1	,,
15	85	−11·0	,,
16	84	−11·9	,,
19	81	−15·5	,,
20	80	−17·0	,,
22	78	−20·0	,,
23·6	76·4	−22·0	Cryohydrate.
25	75	−12·0	Subcryohydrate.
26·27	73·73	0·0	NaCl.
26·5	73·5	+25·0	,, (Poggiale).
26·8	73·2	+40·0	,, (Poggiale).

This Table is to be regarded as replacing Table VI. in § 10 as far as the two are comparable. I bracket the subcryohydrate and the NaCl together, because the range of ratio is so small for a great temperature-difference that I cannot at present undertake to say within two or three degrees the temperature-range peculiar to each body.

§ 128. *Separation of Ice or Anhydrous Chloride of Ammonium from solutions of that salt.*—The following Table (XVII.) shows the temperature of solidification of solutions of NH_4Cl of various strengths.

TABLE XVII.

NH_4Cl per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid.
		°	
1	99	− 0·4	Ice.
3	97	− 1·6	,,
5	95	− 3·1	,,
7	93	− 4·6	,,
10	90	− 7·1	,,
13	87	− 9·9	,,
15	85	−12·0	,,
16	84	−13·0	,,
17	83	−14·0	,,
18	82	−15·0	,,
19	81	−15 8	,,
19·27	80 73	−16·0	Cryohydrate.
20	80	−15	NH_4Cl.
22	78	− 5	,,
23·2	76·8	0	,,
25	75	+ 8	,,
30	70	+32	,,

It will be seen that I make now the solidifying-point of the cryohydrate −16 instead of −15. This agrees with its temperature as a cryogen. The tracing of NH_4Cl in fig. 1 is seen to pass through the 0° line without deflection. Like the NaCl line it has a point of contrariflexure, but not so near the cryohydrate as with the latter salt. The determination at 0° C. was derived from the analysis, 12·1852 of the liquid gave 2·7721 of NH_4Cl.

§ 129. *Separation of Ice or Anhydrous Nitrate of Potassium from solutions of that salt.*—Nitrate of potassium being far less soluble below 0° C. than the two preceding salts, and its cryohydrate not differing much from the saturated solution at 0°, I have not attempted to get any temperature-values between the two; but I have carefully followed the form of the tracing up to the cryohydrate, and also above 0°.

TABLE XVIII.

KNO_3 per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid.
1	99	−0°·1	Ice.
2	98	−0·3	,,
3	97	−0·7	,,
4	96	−1·1	,,
5	95	−1·5	,,
7	93	−2·2	,,
8·5	91·5	−2·6	,,
10	90	−2·9	,,
11·2	88·8	−3·0	Cryohydrate*.
12	88	0·0	KNO_3.
13	87	+2·0	,,
15	85	+6·0	,,
20	80	+14·0	,,
25	75	+21·0	,,
35	65	+35·0	,,
40	60	+41·0	,,

The composition at 0° C. was derived from the analysis by evaporation of 11·8050 grms., which gave 1·4166 of KNO_3, or 12 per cent. (Gay-Lussac found 11·68).

§ 130. *Separation of Ice and Hydrate of* $CaCl_2$ *from solutions of that salt.*—Although troublesome to manipulate, I preferred to make the solutions by weighing the anhydrous chloride

TABLE XIX.

$CaCl_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	0°·2	Ice.
2	98	0·5	,,
3	97	1·1	,,
4	96	1·6	,,
5	95	2·1	,,
7	93	3·3	,,
10	90	5·5	,,
15	85	10·5	,,
20	80	17·5	,,
28	72	27·5	Cryohydrate.
36·45	73·5	37	Unknown hydrate.
39	61	0	$CaCl_2+6H_2O$.
45 (Gerlach)	55	15·5	,,

* I have adopted the temperature −3°, after a long series of experiments, instead of −2°·6, which is given in Table X.

The determination at 0° C. was made by estimating the chlorine as chloride of silver. There is such little difference between the composition of the cryohydrate and the hydrate separated at 0°, that I have been unable to estimate the composition at intermediate temperatures. There is no evidence of the formation of any other hydrate than the one usually regarded as containing six molecules of water. On account of the difficulty of exactly measuring such low temperatures as are here concerned at the maximum, I have less confidence in the exactness of the form of the tracing of this salt than of any other.

§ 131. *Separation of Ice from a solution of Hydrochloric Acid.*—Although I have made a separate study of the hydrogen salts of several of the acids, I may here adduce one instance, namely that of hydrochloric acid, in order especially to compare the forms of the temperature-curve of a body which is, as far as we know, without a cryohydrate *, with the curve-forms of metallic salts, all of which have cryohydrates within the range of artificial cold.

By a silver determination I found that 3·2726 grms. of a pure acid contained 1 grm. of HCl and 2·7734 grms. of water. From this acids of unit percentage weights were formed.

TABLE XX.

HCl per cent. by weight.	H_2O per cent. by weight.	Greatest cold as cryogen.	Temperature at which solidification begins.	Nature of solid.
		°	°	
1	99	.....	− 0·7	Ice.
2	98	.....	− 2·0	,,
3	97	−2·0	− 3·6	,,
4	96	.....	− 5·3	,,
5	95	−2·6	− 7·0	,,
6	94	.....	− 9·0	,,
7	93	−4·0	−11·5	,,
8	92	.....	−14·0	,,
9	91	−4·6	−17·0	,,
10	90	−4·9	−20·5	,,
12	88	−6·2	−27·0	,,
14	86	−7·6	−35·0	,,
16	84	−8·0	−45·0	,,

The tracing of these values is shown on fig. 1, and may be compared with that of spirit of wine derived from the

* A cryohydrate of HCl has recently been described by a French chemist.

numbers given in § 96, Table XI. In neither tracing is there any decided indication of contrariflexure, although the spirit-of-wine tracing passes through its cryohydrate. In the centre column of Table XX. is given the greatest cold when used as cryogens that these acids can produce. The acid was in all cases at 12° C. The great specific heat of the water in which the HCl is dissolved prevents, of course, the attainment of the degree of cold equal to that necessary to solidify a cryohydrate, as is the case with those true salts which do not heat on hydration.

§ 132. *Separation of Ice or Anhydrous Bromide of Potassium from solutions of that salt.*

TABLE XXI.

KBr per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	− 3°	Ice.
20	80	− 7·1	,,
30	70	−12·0	,,
32·15	67·9	−13·0	Cryohydrate.
33	67	− 9·8	KBr.
34	66	− 5·0	,,
35·03	65	0	,,
(Kr.) 39·7	60·3	+20	,,
(Kr.) 43·2	56·8	+40	,,

The solubility at 0° was found from an experiment in which 11·2939 grms. of solution gave 3·9566 grms. of KBr. As Kremers found 34·5, I have adapted his determinations at + 20° and + 40° by adding 0·5 to the numbers he gives.

§ 133. *Separation of Ice and Anhydrous Iodide of Potassium from solutions of that salt.*

TABLE XXII.

KI per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	− 2·2°	Ice.
20	80	− 5·1	,,
30	70	− 9·0	,,
40	60	−14·4	,,
52·07	47·93	−22	Cryohydrate.
55·93	44·07	0	KI.
(Kr.) 58·9	41·1	+20	,,
(Kr.) 61·4	38·6	+40	,,

Having found that 10·3681 grms. of the solution saturated at 0° C. contained 5·7990 of KI, or 55·93 per cent., and since Kremers found 55·86, I have adapted his determination for the 20° and 40° temperatures by adding 0·1 per cent. to his results. The ascent of the tracing (fig. 1) between the cryohydrate and 0° is too abrupt for the insertion of any intermediate value which shall be trustworthy.

§ 134. *Separation of Ice and Anhydrous Sulphate of Ammonium from solutions of that salt.*—The salt was dried at about 100° C., finely powdered, kept at 100° C. for ten hours, and kept for three days and nights in an exhausted receiver over sulphuric acid.

TABLE XXIII.

$(NH_4)_2SO_4$ per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	− 2·6	Ice.
20	80	− 6·0	,,
28·6	71·4	−10·8	,,
40	60	−16·0	,,
41·7	58·3	−17·0	Cryohydrate.
41·9	58·1	0·0	$(NH_4)_2SO_4$.
(H.S.) 43·2	56·8	+19·0	,,

I have for the temperature 19° adopted H. Schiff's determination. Of all the salts which I have examined, the sulphate of ammonium shows in its tracing the greatest precipitousness in its ascent from the cryohydrate to the 0° C. ratio. It is in this region undoubtedly very nearly a straight line. The solubility at 0° C. was found from the data, 13·2512 of the solution gave 5·5522 of the salt obtained anhydrous by the means mentioned above.

§ 135. *Separation of Ice or Nitrate of Ammonium from solutions of that salt.*—The nitrate of ammonium used was dried at 100° C., finely crushed, and heated to incipient fusion; it ceased to lose weight but showed no trace of the nitrite. In the determination of the solubility at 0° C. it was treated in the same manner.

TABLE XXIV.

NH_4NO_3 per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	− 3°·5	Ice.
20	80	− 7·0	,,
30	70	−11·5	,,
40	60	−17·0	,,
43·7	56·3	−17·2	Cryohydrate.
47	53	−12·0	NH_4NO_3.
51	49	− 5·7	,,
54·1	45·9	0·0	,,
(Kar.) 66·5	43·5	+18·1	,,

The solubility at 18°·1 is the observation of Karsten. The shape of the tracing of this salt bears a remarkable resemblance to that of nitrate of potassium (see fig. 1). The gradual slope of its right-hand branch enabled me to insert two determinations there. Also noteworthy is the comparison between the tracing of this salt and that of the sulphate of the same base. Running together with near coincidence down to their cryohydrates, which are nearly identical in temperature and not far apart in percentage of salt, the one rises more abruptly than any other curve; the other is, with one exception, the most gradual.

§ 136. *Separation of Ice and Hydrated Sulphate of Magnesium from the solutions of that salt.*—The analysis of crystallized sulphate of magnesium in regard to its water by direct estimation is rather unsafe, on account of the high temperature required to drive off the last traces of water, and the decomposition of the salt at a somewhat higher temperature. I therefore determined the sulphuric acid in a sample of the sulphate I was about to use, and found that it was nearly the so-called hepthydrate. The determination of the solubility at 0° C. was also derived from a sulphuric-acid determination. Taking every 1·96 grm. of the crystallized salt as containing 1 grm. of $MgSO_4$, the following solutions were examined:—

TABLE XXV.

$MgSO_4$ per cent. by weight.	H_2O per cent. by weight.	Temperature T at which solidification begins.	Nature of solid formed.
5	95	− 0·6	Ice.
10	90	− 1·5	„
15	85	− 3·0	„
20	80	− 4·8	„
21·86	78·14	− 5·0	Cryohydrate.
21·9	78·1	0·0	$MgSO_4+7H_2O$.
25	75	+15·0	„
30	70	+31·0	„

As my determination of the solubility at 0° C. (21·9) differs considerably from some of those given by others (Gay-Lussac 20·5, Graham-Otto 20·5, Pfaff 21·9), I determined for myself the solubilities above 0°.

§ 137. *Separation of Ice or Cryohydrate or Anhydrous Nitrate of Silver from a solution of that salt.*—I have not yet described the temperature and composition of the cryohydrate of this salt. A solution saturated at 0° C. and further cooled gives rise to an abundant crop of iridescent scales, which on examination prove to be the anhydrous nitrate. This continues till −6°·5, when the opaque cryohydrate is formed. The solution, however, is particularly prone to double supersaturation. A solution may sometimes be cooled to −8°; and during this, while the crystals of the nitrate fall, ice-crystals are formed which float. By and by the true cryohydrate is formed on the side of the glass; and then both separate crystallizations cease. This double supersaturation is entirely prevented by introducing a fragment of the previously formed cryohydrate into the mother-liquor which is being further cooled. The temperature remains then constant at −6°·6 to the last drop. The final crop being remelted gave, on analysis, the following results:—14·3538 grms. gave 6·9442 grms. of $AgNO_3$, or 48·38 per cent. of $AgNO_3$ in the cryohydrate. The cryohydrate has accordingly the composition $AgNO_3+10·09\ H_2O$. The temperature −6°·5 is obtained on employing nitrate of silver as a cryogen. There are few more beautiful colourless bodies than the cryohydrate of silver. Opaque, lustrous, and semimetallic, it is somewhat heavier than the liquid in which it is formed.

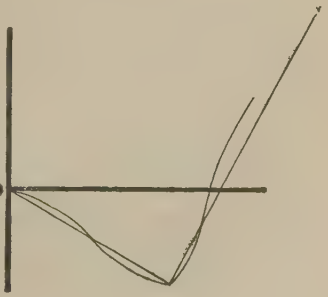
Of a solution saturated at 0° I found that 6·3581 grms. gave 3·5068 of the anhydrous nitrate, or 55·01 per cent. Kremers found 54·9 ; and accordingly I have availed myself of his determinations for the solubilities above 0° C. by adding 0·1 to his percentages.

TABLE XXVI.

$AgNO_3$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid formed.
10	90	− 0·8°	Ice.
20	80	− 2·7	„
30	70	− 4·7	„
40	60	− 6·0	„
48·3	51·7	− 6·5	Cryohydrate.
50	50	− 5·5	$AgNO_3$.
53	47	− 2·2	„
55	45	0·0	„
(Kr.) 69·4	30·4	+19·5	„

§ 138. *Thoughts suggested by* fig. 1.—As the whole field of inquiry contained below the zero-line of fig. 1 has, I believe, remained hitherto unexplored, I am tempted to submit a few remarks upon it. First, of course, the tracings should be continuous curves between 0° and the cryohydrates, and again between the latter and the boiling-point of the saturated solutions, and doubtless, under pressure, beyond. Further, it seems that the curves are all varieties of the same kind. The figure 2 shows what we may liken to the backbone of the curve, with a typical curve about it. There is no absolute measure of what may be called the eccentricity of the curve, because there is no common measure between percentage composition and temperature ; both are measured in arbitrary units. But this does not affect the type or order of the curve's equation. On the left-hand branches there appears to be a point of contrariflexure. The only apparent exceptions to this are KI, alcohol, and HCl. Concerning the two lat-

Fig. 2.



ter, doubtless we only see a fragment of their curves before their final cryohydrates. If there be such a point with KI it must lie between 40 per cent. and the cryohydrate, which is well possible. There seems to be a point of contrariflexure also on the right-hand branch, though sometimes the curvature is so small that this point is practically obliterated. The average slope of descent to the cryohydrate is invariably less than the slope of ascent thence to zero. Indeed every tangent to the left-hand branch of each curve makes a more acute angle with the zero axis than any tangent to the right-hand branch of the same curve. If this be true throughout, the unknown right-hand branch of the HCl curve must be very nearly at right angles to the axis of 0° C. There is no evidence to show that the right-hand branch is continuous with the left-hand. In the case of the halogen salts this almost appears to be distinctly shown not to be the case. If the branches be continuous, it appears that the colder the cryohydrate the less the curvature there. If the branches be discontinuous, the colder the cryohydrate the more acute is the angle between the tangents at the intersection of the curves. This rule holds good in all cases; but between NaCl and KI there is considerable difference of sharpness at the cryohydrate, attending identity of temperature. It is not the case that the deeper the valley the more precipitous the ascent, travelling from left to right; nor is it true that the deepest valley has the widest mouth. That is, salts the most soluble at 0° do not have the coldest cryohydrates, and therefore do not form the most powerful cryogens.

In the shape of the bottoms of the valleys (that is, the curvature about the cryohydrates) the curves of the oxygen salts show a likeness to one another as distinguished from the halogen salts. Considering the former by themselves, we might be inclined to view their two branches as being in all cases continuous. To settle the question decisively whether these curves are continuous, hundredths of degrees would have to be read with precision, and the initial formation of ice noted within that range. If we judge by the aspect of the halogen curves and the general continuity in properties between the halogen and the oxygen salts, I am inclined to consider the two branches discontinuous in all cases.

The tracings assume, of course, somewhat different positions

if they are referred to molecular ratio instead of to absolute-weight ratio. Without determining each tracing for all its intermediate values, we may join by straight lines the points representing the molecular solubility at 0° with the molecular value of the cryohydrate. While each of these lines is, of course, parallel to the corresponding line derived from fig. 1, being got by determining its extremities by division of the percentage by the molecular weight, such division necessarily brings those lines relatively further towards the left whose salts have heavy molecules. The extreme points of the lines are got by dividing the percentage values of fig. 1 by the molecular weights and multiplying by 100. I know no property of the salts here under examination which would have enabled us to predict the position and inclination of these lines. Neither are the water-worths of the salts as cryohydrates nor their solubilities in water at 0° C. in any obvious accord with their known properties.

Correlation between the Boiling and the Glaciation of Salt Solutions.

§ 139. Looking upon the phenomenon of solution as being brought about by the exercise of the force, physical affinity, and regarding the act itself as being in the first instance caused by the prevalence of what may be called physical adhesion (as distinguished from mechanical) between the water and the salt over the sum of the physical cohesions of the water and of the salt, we must after the first contact (that is, when some of the salt is dissolved) regard the contest as between the physical adhesion between the salt and the solution of it on the one hand, and on the other the physical cohesion of the salt together with the physical cohesion of the solution of it. By an increase of temperature the physical cohesion of the salt is lessened. By the solution of more salt the physical adhesion between the salt and the solution is lessened. Thus a partially saturated solution so far resembles what some chemists call a partially saturated atom, that it exhibits not necessarily a lesser energy, but always a lesser capacity for saturation than a still less saturated one. (Witness anhydrous sulphate of magnesium compared with the crystalline salt.) Let us suppose that

at a temperature t° a weight w of water dissolves $\frac{1}{n}$ of s, the weight of the salt. Then using the symbol $\frown$ to denote either physical adhesion or cohesion, we have the condition of equilibrium or saturation expressed by the equation

$$s\left(1-\frac{1}{n}\right)\frown\left(w+\frac{s}{n}\right)=s\left(1-\frac{1}{n}\right)\frown s\left(1-\frac{1}{n}\right)+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right).$$

Or, since the tensions of physical adhesion and cohesion are independent of quantity,

$$s\frown\left(w+\frac{s}{n}\right)=s\frown s+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right).$$

At a temperature t_1°,

$$s\frown\left(w+\frac{s}{n+d}\right)=s\frown s+\left(w+\frac{s}{n+d}\right)\frown\left(w+\frac{s}{n+d}\right),$$

where d is + or − according generally as t_1° is > or < than t°.

The expression

$$s\frown\left(w+\frac{s}{n}\right)>s\frown s+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right)$$

implies that the water is not saturated; while

$$s\frown\left(w+\frac{s}{n}\right)<s\frown s+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right)$$

implies that it is supersaturated. The above equations are the general ones for all salt solutions above 0° C. For temperatures below 0° C. another element manifests itself with greater force as the temperature is lowered, namely the physical affinity between the solid salt and solid water. If in fig. 1 we draw a straight line parallel to and below the zero axis so as to cut any one tracing in two points (it never can be cut in more than two points), we see that solidification may ensue at the same temperature in two differently strong aqueous solutions of the same salt. The intersection with the left-hand branch is the condition of equilibrium resulting from the equality between:—on the one hand, ice $\frown$ ice together with salt $\frown$ water; on the other, salt solution $\frown$ water,

$$\text{ice} \frown \text{ice} + s \frown w = \left(w + \frac{s}{n}\right) \frown w.$$

The intersection on the right-hand branch shows the conditions under which there is equilibrium between :—on the one hand, salt ⌢ salt (or hydrate of salt ⌢ hydrate of salt) together with the salt solution ⌢ salt solution; on the other, salt solution ⌢ salt or hydrate,

$$\text{salt} \frown \text{salt} + \left(w + \frac{s}{n}\right) \frown \left(w + \frac{s}{n}\right) = \left(w + \frac{s}{n}\right) \frown s.$$

Looking upon the cryohydrate as a common value, we have

$$\text{ice} \frown \text{ice} + s \frown s + \text{ice} \frown s = \left(\frac{s}{n} + \frac{w}{m}\right) \frown w + \left(\frac{s}{n} + \frac{w}{m}\right) \frown s.$$

§ 140. Compare now the decomposition of a salt solution by the loss of heat with the decomposition by gain of heat when such a solution boils. And in instituting this comparison, we must bear in mind how much more sensitive to variation in pressure is the boiling- than the solidifying-point.

(1) A solution poorer than the cryohydrate loses heat; ice is formed.

(2) This goes on until the proportion of the cryohydrate is reached, the temperature falling.

(3) The cryohydrate may be reached by freezing out ice from a weaker solution, or by any other withdrawal of water.

(4) When ice separates from a liquid, it remains in contact with the liquid, and endeavours to redissolve therein.

(5) When by the separation of ice the proportion of the cryohydrate is reached (nearly independent of pressure), ice and the salt separate simultaneously.

(6) The two bodies (ice and the salt) being crystallizable

(1) A solution poorer than that saturated at a given temperature receives heat; vapour is formed.

(2) This goes on until saturation is reached, the temperature rising.

(3) Saturation may be reached by evaporation, boiling, or any other withdrawal of water.

(4) Vapour separated from a liquid is removed from the field of contention, unless the liquid be enclosed with the vapour.

(5) When by the separation of vapour the proportion of saturation is reached (very dependent upon pressure), vapour and the salt separate simultaneously.

(6) One being a solid and the other a vapour, they do not

solids, unite to form a crystallizable cryohydrate which exhibits a constant gravimetric composition.

(7) A cryohydrate in the act of solidification shows identity of composition between the solid and liquid portions. The temperature of solidification is constant.

unite, but in their separation preserve a constant gravimetric ratio under like conditions of pressure.

(7) A saturated solution, when boiling, shows the same ratio between the vapour formed and the salt precipitated as exists between the liquid water present and the salt it holds in solution. The temperature of boiling is (under like pressure) constant.

§ 141. A cryohydrate undergoing solidification may therefore be considered physically as the homologue of a saturated salt solution in the act of boiling. For absolute comparison we should have to eliminate pressure, or rather make automatic pressure the measure of the effect of elimination. Wüllner (Pogg. *Ann.* Bd. cx.) found that the vapour-tension of a salt solution varied inversely with the amount of salt it contained. Thus at 51°·8 the vapour-tension of aqueous solutions of chloride of sodium, in mercury pressure, were found to be:—

H_2O.	NaCl.	millim.
100	0	100
90	10	94
80	20	88

Wüllner also found that the diminution of the vapour-tension effected by a given percentage of the salt increases as the vapour-tension increases; that is, the diminution is greater as the temperature is greater. Looking upon vapour-tension as the mechanical equivalent of effort at separation, we find that it has its perfect counterpart in the left-hand branches of the curves of fig. 1. Compare the quantity of vapour with the quantity of ice. The left-hand branches are nearly straight lines; but they are on the whole clearly concave downwards. The variation in the nature of the salt also affects the vapour-tensions; and on constructing the curves of vapour-tension of different salts in solutions of different strengths, we see that the ice-curve is algebraically continuous with the vapour-tension curve. The same may be also seen if we assume that the

atmospheric pressure, being constant, will not affect the order of curvature of the curves representing the ratio of salt in a solution and its boiling-point.

§ 142. The fact that the separate constituents of a solution of the proportion of a cryohydrate are both of one form of matter, of course favours their combination. With boiling aqueous solutions the dissimilarity of the educts is generally unfavourable to their union. There is ample evidence, however, of a similar, though less definite (because more influenced by pressure), reunion of the constituents of certain solutions. If an indefinite quantity of dilute alcohol be rectified 100 times at a constant pressure in such a manner that the first (say half) portion is redistilled, the water is never eliminated, nor does the strengthening extend beyond a definite limit. Perhaps the experiments bearing most directly upon this train of thought are those of Roscoe and Dittmar on the hydration of acids. Since, for instance, nitric acid containing 80 per cent. of HNO_3 is weakened on boiling (considering the residual body), and an acid containing 60 per cent. is strengthened by boiling, until in both cases an acid containing nearly 70 per cent. of HNO_3 is got, which boils at 120° C. at 760 millims., this body was viewed as a definite hydrate. Roscoe showed that this acid, if it be boiled at a lower or higher pressure, is itself decomposed. So with hydrobromic, hydrochloric, and hydriodic acids, with sulphuric acid, and with ammonia. We have here physical ratios conditioned by pressure. Without doubt the cryohydrates would vary in composition if they were formed at enormous pressures; for the variation effected by pressure in the freezing-point of water is not likely to be precisely the same as the variation in the solidifying of a salt out of a solution. Trifling as these differences would assuredly be under all conditions of variation of artificial pressure, the thought is not remote that we may have to refer the extraordinary variation in quantity of the elements of some perfectly well crystallized and constantly composed minerals from what is sometimes called the atomic ratio to the enormous pressure attending their genesis. The fact that such composition may be represented on paper by the complex manipulation of ratios known amongst laboratory products, can only be ad-

mitted into the argument when their formation can be shown in the laboratory by means such as may be fairly supposed to exist in nature. In a word, under vast changes of temperature and pressure, the gravimetric saturating quantities, or "atomic weights," of elementary substances may vary. And it is perhaps noteworthy that this conception, which has urged itself upon us with rare force in the consideration of the relations by weight of bodies in union at extremely low temperatures, is the same as that which has been brought forward by some of those who have examined the relation of the elements when subjected to the high temperature and abnormal pressure of the sun's mass, which has, as a doctrine of continuity, commended itself to some of the most philosophic chemists, and which is certainly in harmony with the conception of dynamic energy, whether of mass or mere velocity.

Our chemistry, as it is generally understood, is the chemistry of one atmosphere pressure.

Separation of Ice from Solutions of Mixtures of Salts.

§ 143. In III. §§ 109–122, I proved that on cooling a saturated solution of two salts, the temperature of the cryohydrate, when reached after separation of various quantities of the constituents, was never sensibly lower than that of the constituent which had the lowest of the two cryohydrate temperatures. In these experiments I was careful to use the salts in such proportion that recombination in integral quantity was possible. In the series of experiments now to be described, where ice has to be separated from a mixture while the salts themselves remain in solution, we may, in those cases at all events where no double decomposition is possible, take equal weights of the salts, so as to compare the results with those of fig. 1; and for this study I will here confine myself principally to the two nitrates $AgNO_3$ and NH_4NO_3, because nitrates are especially free from tendency to form double salts, and because the tracings of the ice-separating temperatures of the individual salts are of widely different range and character.

§ 144. *Separation of Ice from mixed Solutions of the Nitrates of Silver and Ammonium.*—The following are all 20 per cent. solid.

Sol. 1.	$AgNO_3$ . .	20 grms.	gave ice at	$-4{\cdot}3°$.
	NH_4NO_3 . .	10 „		
	H_2O . . .	120 „		
Sol. 2.	$AgNO_3$ . .	20 „	„ „	$-5{\cdot}0$.
	NH_4NO_3 . .	20 „		
	H_2O . . .	160 „		
Sol. 3.	$AgNO_3$ . .	20 „	„ „	$-5{\cdot}5$.
	NH_4NO_3 . .	30 „		
	H_2O . . .	200 „		
Sol. 4.	$AgNO_3$ . .	10 „	„ „	$-5{\cdot}8$.
	NH_4NO_3 . .	20 „		
	H_2O . . .	120 „		

The following are all 30 per cent. solid :—

Sol. 5.	$AgNO_3$ . .	30 grms.	gave ice at	$-6{\cdot}8$.
	NH_4NO_3 . .	15 „		
	H_2O . . .	105 „		
Sol. 6.	$AgNO_3$ . .	30 „	„ „	$-8{\cdot}0$.
	NH_4NO_3 . .	30 „		
	H_2O . . .	140 „		
Sol. 7.	$AgNO_3$ . .	20 „	„ „	$-8{\cdot}9$.
	NH_4NO_3 . .	30 „		
	H_2O . . .	116·6 „		
Sol. 8.	$AgNO_3$ . .	20 „	„ „	$-9{\cdot}1$.
	NH_4NO_3 . .	40 „		
	H_2O . . .	140 „		

On comparing these results with those given in fig. 1 (showing the ice-tracings for the separate salts, which are also 20 and 30 per cent. solid), the following results are obtained in regard to the comparative influences of nitrate of silver and nitrate of ammonium in retaining ice in solution.

TABLE XXVII.

Solution.		Calculated.	Found.
20 per cent.	1. $AgNO_3 = 2$ NH_4NO_3	$-4°{\cdot}1$ C.	$-4°{\cdot}3$ C.
	2. " $= 1$ "	$-4{\cdot}8$	$-5{\cdot}0$
	3. " $= \frac{2}{3}$ "	$-5{\cdot}3$	$-5{\cdot}5$
	4. " $= \frac{1}{2}$ "	$-5{\cdot}5$	$-5{\cdot}8$
30 per cent.	5. " $= 2$ "	$-6{\cdot}9$	$-6{\cdot}8$
	6. " $= 1$ "	$-8{\cdot}1$	$-8{\cdot}0$
	7. " $= \frac{2}{3}$ "	$-8{\cdot}8$	$-8{\cdot}9$
	8. " $= \frac{1}{2}$ "	$-9{\cdot}2$	$-9{\cdot}1$

The calculated numbers are got under the hypothesis that the influences of the constituents of the mixture are proportional to their masses. That is, if there be n grms. of A and m grms. of B, each being a p per cent. solution, and if A alone gives out ice at t_1 and B at t_2, then (t being the temperature at which the mixture gives up ice)

$$t = t_1 + \frac{n}{n+m}(t_2 - t_1);$$

and the numbers found do not differ from those calculated more than may be attributed to errors of observation.

§ 145. *Separation of Ice from the mixed Sulphate and Nitrate of Ammonium.*—Of the 10-per-cent. solution of the sulphate of ammonium 20 grms. were taken; of the 10-per-cent. solution of the nitrate of ammonium 10 grms. were taken. The mixture of these gave up ice at $-3°{\cdot}2$, which is exactly the temperature calculated from the above equation, the glaciating points of the two solutions being $-2°{\cdot}6$ and $-3°{\cdot}5$ respectively. We may assume therefore, generally, that the temperature of glaciation of a mixture of two salt solutions of the same percentage strength is a mean between the glaciation-temperatures of its constituents, when new salts are not formed. This chapter, however, will require a great amount of further work, especially for those cases where the constituent solutions of the mixture are not of the same strength.

§ 146. *Further examination of Iodide of Sodium.*—In conclusion I am very glad to be able to throw a clear light on the anomalous and exceptional behaviour of the iodide of sodium. From §§ 65, 68, 69, it appears that while as a

cryogen this salt gives the temperature $-26°{\cdot}5$, it solidifies as a cryohydrate at $-15°$. A large quantity of the iodide, purified by several recrystallizations, was dissolved to saturation at 12° C., and very gradually cooled to 0°. The crystals given up in this range proved to be anhydrous iodide. On further cooling to $-12°$, a second crop of crystals was formed, which also proved anhydrous. Between $-12°$ and $-20°$ but little further solidification occurred. When $-23°$ was reached rapid solidification began, and the temperature rose to $-15°$. In another similar case the temperature sank to $-24°$ before solidification began. The whole becomes of a dough-like pastiness. The crystals are long, silky needles; they remain transparent. On further cooling in a chloride-of-calcium cryogen to $-26°$, the silvery opacity due to a true cryohydrate is produced, and the whole becomes of a stony hardness. It is clear, therefore, that with the iodide as with the chloride of sodium there are two cryohydrates:—the subcryohydrate, having a melting- and solidifying-point at $-15°$; and another, which in combination with the first has a melting- and solidifying-point at $-26°{\cdot}5$. We have therefore to look for the true (that is, lowest-temperatured) cryohydrate in solutions weaker than that analyzed in § 65, which had 59·45 per cent. With the chloride of sodium there is no difficulty in separating the subcryohydrate; the latter body falls as iridescent scales, and leaves the residual liquid clear. With the iodide of sodium no such mechanical separation ensues, and no artificial separation demanding the maintenance of so low a temperature would be trustworthy.

To get at the composition of the true cryohydrate it must be approached from the other side—not from saturated, but from dilute solutions (see § 123). I have accordingly examined in succession the temperatures at which ice or other body separates from *percentage* solutions of NaI.

TABLE XXVIII.

NaI per cent., by weight.	H_2O per cent., by weight.	Temperature C. at which solidification begins.	Nature of solid separated.
5	95	− 0·7	Ice.
10	90	− 2·1	„
15	85	− 3·9	„
20	80	− 6·0	„
25	75	− 8·5	„
30	70	−11·8	„
35	65	−15·2	„
40	60	−20·5	„
45	55	−26·0	„
49·2	50·8	−30·0	Cryohydrate.
50	50	−29·5	Subcryohydrate.
55	45	−20·0	Subcryohydrate.
60	40	−14·7	„
61·6	38·4	0·0	NaI.
63·6	36·4	+13	„

With regard to the first eight determinations there is nothing particular to remark. For the 40-per-cent. solution a $CaCl_2$ cryogen had to be used. Finding that ice separated from the 45 solution, and the subcryohydrate from the 50 solution, I concluded that the composition of the true cryohydrate must lie between these values. I accordingly submitted several ounces of the 45, and also of the 50 solution to a carbonic-acid cryogen. From the first ice separated; from the second the subcryohydrate. The temperature sank in both cases to −30°, and there remained constant, while from both crop after crop of the pearly-white true cryohydrate was formed. After about three quarters of each had been thus removed, the temperature still remaining at −30°, the residual liquids were analyzed by evaporation and strong heating.

Of 45 solution 10·9945 gave 5·3982 NaI or 49·1 per cent.
Of 60 „ 14·6176 „ 7·1932 „ „ 49·2 „

Accordingly the true cryohydrate is reached from either side. The water worth of this salt is 8·603. It would only be possible to deduce the composition of the subcryohydrate if we knew the relative quantities of the two present, as well as the composition of their compounds. The reason why the dry iodide does not give the temperature of −30° when used as a cryogen is no doubt because, like chloride of calcium, it evolves a large amount of heat in coming into contact with water. But in spite of this deficit, the temperature of the

cryogen is governed, as we have seen it to be before, by that of its coldest constituent. The speculation concerning iodide of sodium in § 69* is fully justified.

For the solubility at 0°, a solution saturated at 8° was kept for three hours at 0° C. Of this, 10·7932 grms. contained 6·6486 grms. of this salt: this gives 61·6 per cent.; Kremers found 61·3.

§ 147. No salt can well be more favourable than the iodide of sodium for the study of double supersaturation. The values of the solution between 49·2 and 61·6 show this phenomenon in a remarkable manner. Thus a solution of 60 per cent. may be kept for hours at −20°. It may be stirred, shaken, particles of dust and particles of NaI may be thrown in, a glass rod covered with a film of hoar-frost inserted, it remains quite limpid. Cooled a few degrees lower, it becomes suddenly semisolid, and rises to −15° or −14° in temperature. At values approaching the cryohydrate, but rather less strong, it may happen, as the excess of water is removed by cold, that instead of the cryohydrate being formed when the right strength is reached, the subcryohydrate is produced continuously with the further separation of ice. The one set of crystals floats, the other sinks. This occasional state of things is the most perfect counterpart of the simultaneous separation of water as vapour and the salt when a saturated solution boils, considered in § 140. A drop or two of the same solution, suddenly cooled to opaque solidification, determines the formation of the true cryohydrate.

I beg the reader to note the following corrections of, and additions to, Table X. § 88. In the case of correction, the corrected number is marked with *, the previously given number being placed in brackets.

Formula of salt.	Temperature of cryogen.	Temperature of solidification of cryohydrate.	Water-worth.	Per cent. of salt.
Add ..... $CaCl_2+3H_2O$	−33	−37	11·8	36·45
Correct... NaI	−26·5	−30*(−15)	8·6	49·2
Correct... NH_4Cl	−16	−16*(−15)	12·4	19·27
Add ..... $AgNO_3$	− 6·5	− 6·5	10·09	48·38
Correct... KNO_3	− 3	− 3*(−2·6)	44·6	11·20

* In this paragraph read "cryohydrate of iodide of sodium" instead of "cryohydrate of sodium."

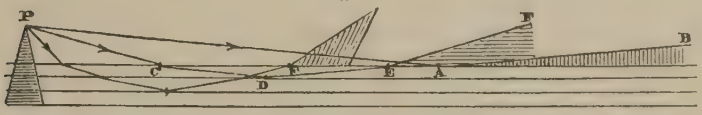
VI. *Remarkable Atmospheric Phenomena in Ceylon.* By *the* Rev. R. Abbay, *M.A.**

One of the most startling and extraordinary of all atmospheric phenomena may be seen during fine weather from the summit of Adam's Peak in Ceylon. This mountain rises extremely abruptly from the low country, and by its elevation of 7200 feet above the sea commands a most extensive and map-like view of all the low lands to the south-west and north-west for a distance of 50 miles or more up to the sea coast. The upper part of the mountain is an acute cone of solid rock, some 2000 feet or more in height, that rises in perfect isolation above the range of which it forms a part, and also above all the neighbouring mountains to the east and north. The phenomenon, which is described by all who have witnessed it as of the most striking character, is seen at sunrise, and consists *apparently* of an enormous elongated shadow of the mountain projected to the westward, not only over the land but over the sea, to a distance of 70 or 80 miles. As the sun rises higher it rapidly approaches the mountain, and appears at the same time to rise before the spectator in the form of a gigantic pyramid of shadow. Distant objects, a hill or a river (or even Colombo itself, at a distance of 45 miles), may be distinctly seen through it, lighted up by the sunlight, diffused most probably by the surrounding illuminated atmosphere; so that the shadow is not really a shadow on the land, but a veil of darkness suspended between the observer and the low country. All this time it is rapidly rising and approaching, and each instant becoming more distinct, until suddenly it seems to fall back on the spectator, like a ladder that has been reared beyond the vertical; and the next instant it is gone. Of the accuracy of the above facts I have no doubt whatever. A great number of trustworthy witnesses have described it to me; and but for a sudden attack of fever at the foot of the peak, which prevented an ascent being made in the evening, I should have been able to describe it from personal observation. As it was I ascended next day and was able to form a very good idea of the conditions under which the phenomenon takes place; but I was, of course, unable to

* Read May 27, 1876.

obtain accurate data as to the duration of the veil, the height to which its apex rises above the horizontal, the elevation of the sun, &c. If I am right in supposing that no explanation has ever been offered of this remarkable appearance, the following remarks, which appear to be fairly satisfactory, may perhaps not be uninteresting. The average temperature at night in the low country, during the dry season when Europeans ascend the mountain, is between 70° and 80° F., whilst that on the summit of the peak is from 30° to 40° F. Consequently the lower strata of air are much less dense than the upper ; and an almost horizontal ray of light passing over the summit, must of necessity be refracted upwards and suffer total internal reflection as in the case of an ordinary mirage. This may be readily seen by a reference to fig. 1, where a

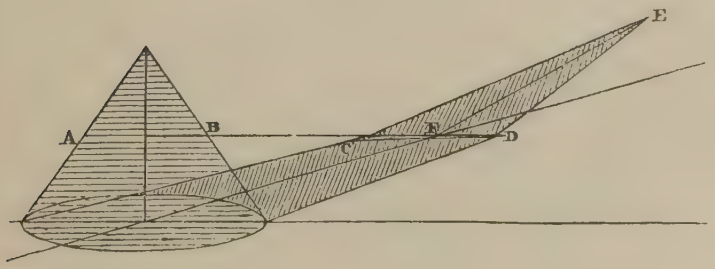
Fig. 1.



nearly horizontal ray passing over the summit of the peak P suffers total internal reflection at A, and is deviated upwards in the direction A B ; or when a less horizontal ray is refracted at C, reflected at D, and refracted again at E, it finally issues along the line E F. It will be evident from fig. 1 that the shaded parts represent the veil of darkness at three different moments of time, and also that the veil appears to rise as its base approaches the mountain, *i. e.* as the sun rises and the rays fall less horizontally.

By referring to fig. 2 it will be seen how the aerial shadow

Fig. 2.



of the upper part of the peak, *i. e.* the part above A B, suffers total internal reflection, and is thrown upwards into the air as C E D. It will also be evident, by comparing the two figures, that as the veil of darkness approaches it must tend to assume a more vertical position until it reaches the critical angle when total internal reflection ceases and the veil suddenly disappears. Its apparent tilting over on the spectator I imagine to be merely an illusion produced by the rapid approach and rising of the dark veil without any gradual disappearance which can be watched and estimated. It will be evident that it is the illumination of the innumerable particles floating in the atmosphere, and capable of reflecting light, that causes this aerial shadow to be visible by contrast.

Another atmospheric phenomenon visible in Ceylon, of great interest but not so striking in character as the above, admits of an equally simple explanation. Not unfrequently in the mountain districts broad beams apparently of bluish light may be seen extending from the zenith downwards, converging and narrowing as they approach the horizon. This ray-like appearance is very similar to that seen before sunrise; only the point from which the rays proceed is *opposite* the sun: the rays themselves are very broad and blue in colour; and the spaces between them have the ordinary illumination of the rest of the sky. If we suppose in this instance that the lower strata of air are colder than the upper (a condition of the atmosphere which not unfrequently occurs in a tropical mountain district like that of Ceylon, where large currents of heated air sweeping up a valley cross another valley nearly at right angles and at a considerable elevation above it), the refraction spoken of in the case of Adam's Peak will be downwards instead of upwards. If, too, the observer be *below*, the veil of darkness will appear to him like a very elongated triangle apex downwards, or broad ray, through which the blue sky beyond may be seen free from the palish illumination of the atmosphere, whilst on either side the ordinary illuminated sky will be seen. If now we suppose several isolated masses of cloud to partially obscure the sun, as was the case when I witnessed the phenomenon, we may have several corresponding inverted veils of darkness, like blue rays in the sky, all apparently converging towards the same point below the horizon. This apparent convergence

of the beams is merely an effect of distance, as in the case of parallel rays of light from the rising or setting sun, the blue rays being practically parallel bands in the atmosphere devoid of illumination. It will be evident that conical-shaped clouds are not necessary to produce this effect. Isolated clouds of any massive form would be sufficient to throw the bands of shadow through the illuminated atmosphere, and refraction and perspective would do the rest. The above phenomenon is called by the Singhalese "Buddha's rays;" and though according to Sir Emerson Tennent it is very varied in character and appears in different parts of the sky, yet I have only seen it when the sun was low at evening and when the rays converged to a point, apparently directly opposite the sun; and I do not think it possible for the phenomenon to be seen in any other position.

VII. *Model of a small Electrical Machine.*

By GEORGE FULLER, *C.E., Belfast**.

THIS machine is a double-acting electrophorus worked by cranks, with the addition of an arrangement by which a small electric charge given to it is augmented and kept up, so that the dielectric does not require to be recharged.

A is a vulcanite plate supported in a vertical position by two insulated standards, p, p.

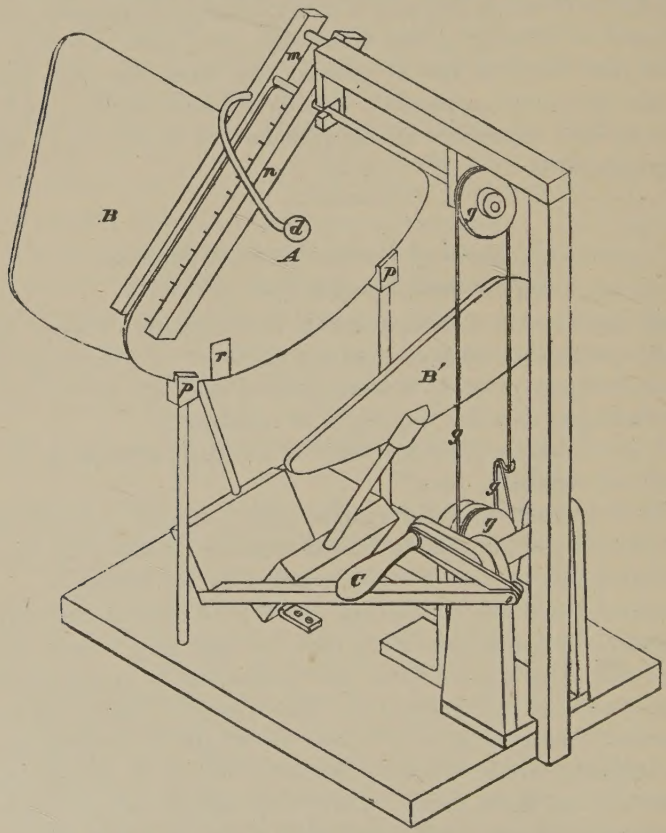
B, B′ are two insulated metallic plates, one on each side of the plate A; these can be moved together to and from contact with A by means of cranks worked by the handle C.

m and n are two conductors armed with needles and connected by means of two glass rods, so that they receive the same reciprocal motion from the mechanism by means of the wire, cord, and pulleys, g, g, g. The wire g is attached to the arm that moves the plate B′; and the length of the cord and size of pulley are so adjusted that when this is in its extreme position from A, as shown, m and n are also at one extremity of their motion, as shown; and when B and B′ are in contact with A, m and n are horizontal. The conductor n is not insulated; and it will be seen by the diagram that m and n during their motion pass on either side of the plate A.

* Read June 24, 1876.

To the conductor m is fixed a wire terminating in a brass ball, d; this wire is of such length and form that when B and B′ recede from A, and m and n move downwards from their horizontal position, the ball d passes close to B′. Care has to be taken that this juxtaposition does not occur until the vulcanite plate separates the points on m and n.

The action of the instrument is as follows:—A charge of, say, negative electricity having been given to the insulated arm m when in a vertical position, on motion being given to



the machine this electricity is distributed by means of the points over the face of the vulcanite next to B; at the same time positive electricity is drawn from the earth, thrown upon the other face of that plate by the uninsulated points attached

to n. When now B and B′ are brought into contact with A, the negative electricity on its one face attracts the positive on the conductor B and repels the negative, whilst the positive on its opposite face attracts the negative on the conductor B′ and repels the positive; then, by means of the piece of tinfoil (r) that connects B and B′ when they are in contact with A, the two electricities that are repelled neutralize each other; and when the plates are moved away from the vulcanite, B is charged with positive and B′ with negative electricity. Then, before reaching its extreme position, the latter communicates its charge to the insulated arm m by the brass ball d, and its negative electricity is thus distributed over the surface of A next to B and thus augments its original charge. At the end of its path B′ is momentarily connected to earth. It will be evident that on again bringing the plates into contact the charge in B is augmented; also that if a supply of negative electricity is required, the only modification of the above is to give to m a charge of positive instead of negative electricity.

The above instrument forms an easily constructed and worked electrical machine, and is beside interesting as rendering automatic the classical electrophorus of Volta.